SOME ASPECTS OF THE STRUCTURAL CHEMISTRY OF THE GROUP IIIA ELEMENTS

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KEY TO ABBREVIATIONS

acac	acetylacetonate
ttfacac	thienyltrifluoroacetylacetonate
tfacac	trifluoroacetylacetonate
ϕacac	benzoylacetonate
$\phi_2$acac	dibenzoylmethanate
tropo	tropolonate
dtc	N,N-diethyldithiocarbamate
2-Sox	pyridine-N-oxide-2-thiolate
pic	picolinate
6-Mepic	6-methylpicolinate
8q	8-hydroxyquinolinate
2-Meox	2-methyl-8-hydroxyquinolinate
ϕ_3P	triphenylphosphine
bipy	2,2'-bipyridyl
terpy	2,2',2''-terpyridyl
phen	1,10-phenanthroline
tmen	N,N,N',N'-tetramethylethylenediamine
MeMe'dpma	methyl-(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine
$[GaMeMe'dpmaCl(OH)]_2^{2+}$	di-μ-hydroxo-bis[chloro(methyl-(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine
pmtc	pentamethylenedithiocarbamate

Key to Abbreviations, continued . . .

mnt	1,2-dicyanoethylenedithiolate
gly	glycinate
CrC_3N_3	*fac*-diethylenetriaminechromium tricarbonyl
dcbtc	N,N-di-t-butyldithiocarbamate

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Synthetic and structural studies of gallium(III) coordination complexes were undertaken. Tris complexes of gallium(III) with monoanionic bidentate ligands are readily prepared from gallium trichloride and the sodium salt of the ligand in a suitable non-aqueous solvent.

The crystal and molecular structures of tris(acetylacetonato)gallium(III) and tris(acetylacetonato)indium(III) have been determined. The average metal-oxygen distances in these nearly ideal octahedral complexes are 1.952(7) Å and 2.132(5) Å respectively. The acetylacetonates of gallium(III) and indium(III) are compared with those of other tripositive metal ions and correlations between metal-oxygen distance, ionic radius, oxygen-oxygen inter-ligand contacts and ligand bite are discussed.

The crystal and molecular structure of tris(N,N-diethyldithiocarbamato)gallium(III) has been determined and the average gallium-sulphur distance is 2.435(3) Å. The complex is extremely distorted from ideal octahedral geometry which is discussed in terms of ligand bite and metal size.

The crystal and molecular structures of tris(thienyltrifluoroacetylacetonato)gallium(III), tris(picolinato)gallium(III) monohydrate and tris(6-methylpicolinato)gallium(III) have been determined and the compounds are trans octahedral species. An interesting and recurring feature in these compounds is a rigid effect caused by steric interactions. Steric effects cause ligands in the same complex to distort differently and this, in turn, causes the cis effect. These various distortions are attributed to the maintenance of electroneutrality on the metal.

The crystal and molecular structures of trichloro(2,2',2''-terpyridyl)indium(III) and thallium(III) have been determined and these compounds are trans octahedral species. When compared with trichloro(2,2',2''-terpyridyl)gallium(III), one sees the effect of increasing metal size in an isomorphous and chemically similar series of compounds. With increasing metal size, the steric effects most pronounced in trichloro(2,2',2''-terpyridyl)gallium(III) decrease. A trans effect is noted in this series of complexes.

The crystal and molecular structure of chlorobis(2-methyl-8-hydroxyquinolinato)gallium(III) has been determined and it is the first example of a trigonal-bipyramidal gallium(III) complex characterized by x-ray diffraction. The complex has nitrogen atoms in the axial positions and the chlorine and two oxygen atoms in the equitorial positions. The stability of the complex is related to steric effects.

We have also characterized the first hydroxo-bridged gallium(III) complex, di-μ-hydroxo-bis[chloro(methyl-(6-methyl-2-pyridylmethyl)-(2-pyridylmethyl)amine)gallium(III)]chloride monohydrate. The octahedral geometry about the metal shows a trans effect similar to trichloro(2,2',2''-terpyridyl gallium(III). However, this can also be rationalized in terms of steric interactions.

Twist angles were calculated for several octahedral and bicyclopentadienyl complexes. The magnitude of the angle is dependent on the mode of calculation, except when the metal lies on the line joining the centroids of the n-fold faces (n = 3,5) and the n-fold faces are parallel. These factors should be checked and quoted when one calculates twist angles. In general, idealized geometries and the relationships derived from them are not valid.

CHAPTER I

INTRODUCTION

The group IIIA elements are one of the most elegant [illegible] the periodic law. In 1868 Mendeleev correctly showed that indium, which had been recently discovered in 1863 by Reich and Richter, belonged in the same group of elements as boron, aluminum and thallium[1]. Subsequently, in 1871, Mendeleev predicted the existence of certain elements[2] based on absences in his periodic table. One of his predictions was eka-aluminum, an element which should exist after zinc and between aluminum and indium in that table. This was substantiated in 1875 by Boisbaudran[3] and the new element was given the name gallium. With experimental verification, the periodic law became accepted and has since become a cornerstone of chemical thought.

The group IIIA elements are boron, aluminum, gallium, indium and thallium. All are considered to be metals except boron. These elements exist predominantly in the trivalent oxidation state, except thallium, where the univalent state is stabilized by the inert pair effect[4]. The group forms stoichiometric oxides, halides, alkyls and hydrides. As a result, these elements seem extremely similar. This, to a certain extent, is reflected in their physical properties listed in Table 1.

From Table 1, it can be seen that gallium has an abnormally small size and large Allred-Rochow electronegativity. Gallium, therefore,

Table 1 — Selected Physical Properties of the Group IIIA Elements

Property		Element					
		B	Al	Ga	In	Tl	ref
Ionic Radius (Å)							
4 coordinate	Ionic Radius	.12	.39	.47			
	Covalent Radius	.26	.53	.61			5
6 coordinate	Ionic Radius		.53	.62	.79	.880	
	Covalent Radius		.67	.76	.93	1.020	
(for trivalent ions)							
Electronegativity							
Pauling		2.04	1.61	1.81	1.78	2.04	6
Allred-Rochow		2.01	1.47	1.82	1.49	1.44	7
Sanderson		1.88	1.54	2.10	1.88	1.96	8
Mulliken-Jaffe'		1.81	1.64	1.82	1.57		9
Ionization Potentials							
first		8.298	5.986	5.999	5.786	6.108	10
second		25.154	18.828	20.51	18.869	20.428	
third		37.350	28.447	30.71	28.03	29.83	

would not be expected to behave quite like aluminum, indium or thallium. This is revealed in a comparison of their hydrides and chlorides. Gallane is a molecular dimer similar to diborane, while aluminum and indium hydrides are polymeric.[11] Similarly, gallium trichloride exists in the solid state as Ga_2Cl_6, a molecular dimer.[12] Aluminum, indium and thallium trichloride, by contrast, exist as ionic solids with a rhombic chloride type structure.[13] As a result, we should expect gallium to be similar to aluminum, indium and thallium, but with certain subtle and distinct differences due to anomalous size and electronegativity.

The synthetic coordination chemistry of all the group IIIA metals has been slow to develop. This dearth of activity was due to a variety of reasons: i) the rareness of gallium and indium, ii) the ease of reduction of Tl(III), iii) the hygroscopic nature of most Al(III) complexes and, iv) the lack of spectroscopic techniques for studying these complexes. With the discovery of Ziegler-Natta catalysis and use of aluminum trichloride as a Friedel-Crafts reagent, group IIIA chemistry in general received much more attention. Simultaneously, the development of transistor technology made both gallium and indium available at a moderate price. Concurrent with these events has been the development of sophisticated spectroscopic methods with which the coordination complexes of group IIIA can be studied.

The first coordination complex of gallium(III) to be synthesized was the tris-acetylacetonate.[14] Morgan and Drew were able to prepare this in 1922 after the death of Dr. J.H. Pollok who bequeathed a 0.12 g sample of the pure metal to Gilbert Morgan. Delepine later prepared

several carbamates and xanthates.[15,16] In the late forties, Irving prepared several oxinates and substituted oxinates of gallium(III) to test them as analytic precipitants for the metal.[17] In the last two decades, Greenwood and coworkers have studied extensively gallium(III) halide complexes and, to a lesser degree, gallane and organogallium compounds.[18] Complexes with ethers, thioethers, phosphines and especially amines and pyridines were studied. Subsequently, Carty and coworkers prepared the 2,2'-bipyridyl[19] 1,10-phenanthroline,[20] 2,2',2''-terpyridyl[21] and other polyamine[22] complexes of the gallium(III) halides.

Recently, Tuck and coworkers have studied a variety of halide and pseudohalide complexes of indium with a host of oxygen, nitrogen, phosphorous and sulphur ligands.[23] Walton has prepared several pyridyl and polypyridyl complexes with both indium and thallium trichlorides.[23,24] Cotton and Johnston have prepared dimethylsulphoxide and 2,2'-bipyridyl complexes of thallium trichloride.[25] Nyholm and Ulm have prepared a number of arsine complexes of gallium and indium trihalides.[26] Due to these studies, a moderate number of complexes are known.

The methods of characterizing these complexes have ranged from conductivity measurements to vibrational spectroscopy to x-ray diffraction. The first method is unsatisfactory because i) ionization may occur in solution, ii) an appropriate solvent may be unavailable and iii) the Onsager law holds only in the limit of infinite dilution; therefore, extrapolation to a meaningful limit may be impossible.[27] Vibrational spectroscopy, while often useful, can be ambiguous. Classic examples of this are the 2,2',2''-terpyridyl complexes of the aluminum, gallium, indium and thallium trihalides.[21]

All of these complexes have only two metal-halogen stretching frequencies, although group theory predicts three modes for a trans octahedral species. Thus, absences of bands in vibrational spectroscopy need not imply their nonexistence. Therefore, care should be taken in assigning structures on the basis of such evidence. X-ray diffraction is clearly the superior method. It, too, however, suffers a certain drawback, namely the substance must be crystalline.

The structural chemistry of group IIIA is quite large in certain areas. A great deal of work in both x-ray and neutron diffraction has been done on alums.[28,29] Similarily, hydrides and some of their amine complexes have been studied. Several organometal compounds and various adducts also have had their structures determined.[30] The halides and halo-amines of the group IIIA metals have received a great deal of attention too.[31,32]

By comparison, little work has been done on the structural aspects of acieceler or halide coordination complexes of the group IIIA metals. For aluminum, the tris oxotyarrtonatr[35] structures have been solved, as has been the very interesting five coordinate oxo-bridged complex bis(2-methylquinolinato)[36] aluminum(III)-oxo-bis(2-methylquinolinato) aluminum(III). The structures of four-coordinate aluminum trihalide complexes with such Lewis acids as propionylchloride or o,m or p-toluyl chloride are also known.[37,38]

Kennard determined the first gallium(III) coordination complex,[39] hydrogenethylenediaminetetraacetatoaquagallate(III), which is an octahedral zwitterionic complex. Palenik and coworkers have also solved the structures of $GaCl_3$ (2,2' - bipyridyl)[40] and $GaCl_3$ (2,2',2'-terpyridyl)[41] The former is the lonir species cis-dichlorobis(2,2'-

bipyridyl)gallium(III) tetrachloregallate, while the latter is a trans-octahedral species. Tetrahedral and octahedral seem to be the preferred geometries for gallium(III).

With Indium(III), three types of coordination complexes have had their structures studied. The first type is represented by InL_3(dimethylsulphoxide)$_2$[42] which is cis-diiodotetrakis(dimethylsulphoxide) indium(III) tetraiodoindate. The second type, represented by $InCl_3 \cdot bis$(triphenylphosphine),[43] is a monomeric molecular trigonal bipyramidal species. The third type is represented by InL_3, L = N,N-diethyldithiocarbamate,[44] pentamethylenedithiocarbamate,[45] dimethyldithiophosphinate[46] and dithiophenylacetate.[47] This latter type is a series of distorted six coordinate species. It is interesting to note that aluminum and Indium easily form five coordinate species, while gallium forms only four or six coordinate complexes. Only one coordination complex of thallium(III), $TlCl_3$(1,10-phenanthroline)[48] has had its structure determined. The structure is a chloride bridged six-coordinate dimer.

Previous work has shown that the group IIIA metals form a variety of coordination polyhedra. Furthermore, gallium(III), by virtue of its small size and large electronegativity, is unique amongst the other elements of the group. In order to understand more about gallium(III)'s uniqueness and similarity in group IIIA, this study has been undertaken.

CHAPTER 2

SYNTHESES AND CHARACTERIZATION

Reactions employing gallium and indium trichloride were done under anhydrous conditions. All glass apparatus was oven dried and not allowed to stand in air. Acetonitrile and methanol were dried over phosphorous (V) oxide and magnesium methoxide, respectively, and were freshly distilled before use. Gallium trichloride was sublimed in vacuo onto dried acetonitrile at liquid nitrogen temperature. Indium trichloride was added to dry solvents from pre-weighed vials. The reactions were carried out quickly in air and worked up without any precautions taken to avoid moisture. In virtually all cases, no hydrolysis of the reaction product occurred.

Gallium trichloride, gallium nitrate octahydrate and indium metal (99.99% purity) were purchased from Fluka, A.G. Buchs, Switzerland. The former was in a sealed ampoule which was attached to a vacuum line before use. Other chemicals and their suppliers are 8-hydroxyquinoline, Fisher Scientific, Fair Lawn, N.J., indium perchlorate nonahydrate, G. Frederick Smith Chemical Co., Columbus, Ohio, acetylacetone, Mallinckrodt, Coleman and Bell, Norwood, Ohio, benzoylacetone, trifluoroacetylacetone and hexafluoroacetylacetone, Columbia Organic Chemical Co., Inc., Columbia, S.C., and dibenzoylmethane, thenoyltrifluoroacetone, tropolone, 2-picolinic acid, 6-methyl-2-picolinic acid, 2-methyl-8-hydroxyquinoline and sodium N,N'-diethyldithiocarbamate trihydrate, Aldrich Chemical Co., Inc., Milwaukee, Wisconsin.

All solvents were reagent grade and used without any further treatment, unless otherwise specified. Infrared spectra were recorded on a Beckman IR-10 spectrometer as nujol mulls. Nmr spectra were recorded on a Varian A60A spectrometer, using deuterated chloroform as a solvent and TMS as an internal standard. Mass spectra were recorded on an MS 30 mass spectrometer with perfluorokerosene as a mass marker or on a Hitachi-Perkin Elmer mass spectrometer. Melting points were determined on a Mel-Temp melting point apparatus in open capillaries and are uncorrected. Micro-analyses were done by Galbraith Laboratories, Knoxville, Tennessee.

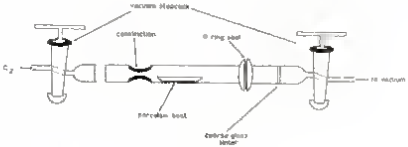


Figure 1. Apparatus for $InCl_3$ Synthesis

Syntheses

Indium trichloride

Indium trichloride was prepared by a modification of Carry's method.[49] Indium metal (1.0g, 8.7 mmoles) in a porcelain boat was placed in the apparatus shown in Figure 1. The system was then evacuated, flamed and placed in a tube furnace at 220°C. Chlorine was introduced and indium trichloride sublimed out of the hot zone. When the reaction was complete, the apparatus was again evacuated, then sealed and separated

at the constriction. The halide-containing portion was opened in a dry-box and the anhydrous halide was then placed in pre-weighed vials which were then sealed. Yield: 1.6g, 85%

Sodium Acetylacetonate

Sodium acetylacetonate was prepared by the reported synthesis [50]. Sodium (2.1g, 90mmoles) was dissolved in absolute ethanol (60ml) and to this was added acetylacetone (9g, 90mmoles) producing an immediate white precipitate. Diethyl ether (100 ml dried over calcium hydride) was then added and the mixture was refrigerated overnight. The white crystalline solid was then filtered, dried in vacuo and stored in a sealed container which was then refrigerated. Yield: 7g, 64%.

Tris(acetylacetonato)gallium(III)

Gallium trichloride (1.30g, 7.38 mmoles) in dry acetonitrile (40 ml) was added to a hot solution of sodium acetylacetonate (2.70 g, 22.1 mmoles) in absolute ethanol (60 ml). An immediate white precipitate formed and was filtered off. The solvent was stripped from the filtrate, leaving a bright orange solid. Recrystallization from methanol produced well-formed, plate-like crystals.

Tris(acetylacetonato)indium(III)

Indium trichloride (1.29g, 5.85 mmoles) in dry methanol (50 ml) was added to a hot solution of sodium acetylacetonate (2.14g, 17.6 mmoles) in dry methanol (20 ml). Copious amounts of a white precipitate formed and the solution became light green in colour. The white precipitate was filtered off and the filtrate, on standing, produced large, clear, colourless, cubic crystals.

Tris(thienoyltrifluoroacetylacetonato)gallium(III)

Gallium trichloride (1.00g, 5.71 mmoles) in dry acetonitrile (40 ml) was added to a hot, bright lime coloured solution of thenoyltrifluoroacetone (3.81g, 17.2 mmoles) and sodium methylate (0.94g, 17 mmoles) in dried methanol (120 ml). A deep purple solution formed and, with further heating, produced a white precipitate which was filtered off. The solvent was then stripped from the filtrate, leaving a rose coloured solid. Recrystallization from methanol gave well-formed, plate-like crystals.

Tris(thienoyltrifluoroacetylacetonato)indium(III)

Indium trichloride (0.90g, 2.7 mmoles) in dry methanol (20 ml) was added to a hot, bright lime coloured solution of thenoyltrifluoroacetone (1.81 g, 8.17 mmoles) and sodium methylate (0.44g, 8.2 mmoles) in dry methanol. A rose coloured solution formed and the solvent was stripped, leaving a rose coloured solid. Recrystallization from methanol produced large, orange, multifacial crystals.

Tris(trifluoroacetylacetonato)gallium(III)

Gallium trichloride (0.90g, 5.1 mmoles) in dry acetonitrile (50 ml) was added to a hot, yellow solution of trifluoroacetylacetone (2.64g, 15.3 mmoles) and sodium methylate (0.81, 15 mmoles) in dry methanol (100 ml). The solution turned deep orange in colour, it was then filtered and the solvent stripped from the filtrate, leaving an orange crystalline residue. Recrystallization from methanol produced well formed, diamond-shaped, plate-like crystals.

Tris(benzoylacetonato)gallium(III)

Gallium trichloride (2.38g, 13.5 mmoles) in dry acetonitrile (28 ml) was added to a hot, green solution of benzoylacetone (8.56 g, 40.5 moles) and sodium methylate (2.19 g, 40.5 mmoles) in dry methanol (100 ml). A deep brown transient colour was produced and faded to a bright orange colour as copious amounts of a white precipitate were produced. The mixture was filtered and the solvent stripped from the filtrate, leaving an orange powder which was recrystallized from chloroform.

Tris(dibenzoylmethanato)gallium(III)

Gallium trichloride (2.38g, 13.5 mmolow) in dry acetonitrile (28 ml) was added to a hot, orange-green solution of dibenzoylmethane (9.08g, 40.5 moles) and sodium methylate (2.19g, 40.5 moles) in dry methanol (100 ml). A deep red transient colour formed, which gave way to a bright orange colour as copious amounts of a white precipitate were produced. The mixture was filtered and, upon standing, the filtrate produced an orange crystalline solid.

Tris(tropolonato)gallium(III)

Gallium nitrate octahydrate (2.1g, 5.1 mmoles) in methanol (50 ml) was added to a hot, bright yellow solution of tropolone (1.83g, 15.2 mmoles) and sodium methylate (0.8g, 15.2 moles) in methanol (100 ml). A white precipitate formed immediately and was filtered off. Recrystallization from chloroform gave clear, colourless, needle-like crystals. Unfortunately, the crystals turned opaque when removed from their mother liquor.

Ammonium tris(oxalate)gallate(III)

Sodium hydroxide (0.70g, 18 mmoles) in deionized water (12 ml) was added to a solution of gallium nitrate octahydrate (2.30g, 5.75 mmoles), immediately forming a gel-like precipitate. To this was added a freshly boiled solution of ammonium oxalate monohydrate (1.22g, 8.60 mmoles) and oxalic acid dihydrate (1.09 g, 8.60 mmoles) in deionized water (25 ml). After 20 ml of the latter solution were added, most of the gel-like precipitate dissolved. The slightly turbid mixture was then filtered through celite and the filtrate produced huge, plate-like crystals upon standing.

Tris(N,N-diethyldithiocarbamate)gallium(III)

Gallium trichloride (1.00g, 5.71 mmoles) in dry acetonitrile (40 ml) was added to a hot solution of sodium N,N-diethyldithiocarbamate trihydrate (3.85g, 17.1 mmoles) in dry acetonitrile (80 ml). The mixture turned dark gray and formed a white precipitate which was filtered off. The filtrate, upon standing, produced well formed cubic crystals.

Tris(pyridine-N-oxide-2-thiolate)gallium(III)

Gallium trichloride (1.60g, 9.08 mmoles) in dry acetonitrile (30 ml) was added to a hot solution of the salt of 2-mercaptopyridine-N-oxide (4.07g, 27.3 mmoles) in dry methanol (150 ml). Copious amounts of a light gray precipitate were produced immediately, filtered off, washed successively with 95% ethanol and diethyl ether, then dried *in vacuo*.

Tris(picolinate)gallium(III)monohydrate

Gallium trichloride (2.20g, 12.5 mmoles) in dry acetonitrile (50 ml) was added to a hot solution of picolinic acid (4.62g, 37.5 mmoles) and

sodium methylate (2.04g, 37.8 mmoles) in dry methanol (125 ml). Transient red and then yellow colours formed, giving way to a lime-green colour as a fine, white, crystalline precipitate was generated. The mixture was filtered and, on standing, the filtrate produced a copious amount of a white, fibrous material. This mixture was allowed to stand for two days, during which time the fibrous material dissolved. Then the solution which formed produced clear, colourless, plate-like crystals.

Tris(6-methylpicolinate)gallium(III)

Gallium trichloride (1.60g, 9.09 mmoles) in dry acetonitrile was added to a hot solution of 6-methylpicolinic acid (3.74 g, 27.3 mmoles) and sodium methylate (1.47g, 27.2 moles) in dry methanol (120 ml). An immediate white precipitate formed and was filtered off. On cooling, the filtrate produced clear, colourless, cubic crystals.

Tris(8-hydroxyquinolinate)M (M = aluminum(III), gallium(III), indium(III))

These complexes were prepared by reacting stoichiometric amounts of the metal ion in aqueous solution with 8-hydroxyquinoline in 95% ethanol. Immediately, bright green precipitates formed which were filtered off, washed successively with 95% ethanol and diethyl ether and dried in vacuo.

Tris(2-methyl-8-hydroxyquinolinate)aluminum(III)

Aluminum trichloride (1.36g, 10.2 moles) in deionized water (100 ml) was heated and added to a hot solution of 2-methyl-8-hydroxyquinoline (4.87g, 30.6 moles) in methanol (50 ml to give a fluorescent, yellow-green solution. A bright, yellow-green precipitate formed on the

addition of 2N aqueous sodium acetate (100 ml). The precipitate was filtered off and recrystallized from methanol.[51]

Tris(2-methyl-8-hydroxyquinolinato)gallium(III)

Gallium nitrate octahydrate (2.0g, 5.0 mmoles) in hot deionized water (100 ml) was added to a solution of 2-methyl-8-hydroxyquinoline (2.39g, 15.0 mmoles) in deionized water (60 ml). A bright green solution formed, which produced a green precipitate when 2N aqueous sodium acetate was added (100 ml). The mixture was digested for 3 hours, then the precipitate was filtered and recrystallized from chloroform.

Tris(2-methyl-8-hydroxyquinolinato)indium(III)

a) Indium perchlorate nonahydrate (3.0g, 4.31 mmoles) in hot distilled water (30 ml) was added to a hot solution of 2-methyl-8-hydroxyquinoline (2.34g, 14.7 mmoles) in methanol (30 ml). Aqueous sodium acetate (30 ml, 2N) was added to this green solution, forming a green precipitate which was digested, filtered, and recrystallized from chloroform.

b) Indium trichloride (0.95g, 2.6 mmoles) in dry acetonitrile (30 ml) was added to a hot solution of 2-methyl-8-hydroxyquinolinol (1.25g, 7.80 mmoles) and sodium methylate (0.49g, 7.8 mmoles) in dry methanol (30 ml). A yellow-green solution formed which, when cooled, gave well formed, green, plate-like crystals.

Chlorobis(2-methyl-8-hydroxyquinolinato)gallium(III)

Gallium trichloride (0.82g, 4.7 mmoles) in dry acetonitrile was added to a hot solution of 2-methyl-8-hydroxyquinolinol (2.23g, 14.1 mmoles)

and sodium methylate (0.76g, 14.1 moles in dry methanol (100 ml). A deep green solution formed as a white precipitate was produced. The mixture was filtered and the solvent then stripped from the filtrate, leaving a green solid. Recrystallization from chloroform gave large, well formed, green, plate-like crystals.

Characterisation

Analyses are given in Table 2A and agree well with formulated stoichiometries. Molecular weights were determined, where possible, from mass spectrometry and are given in Table 3B. Nmr (^1H) spectra are listed in Table 3 for those compounds soluble in chloroform. The infra-red spectra of most of these complexes were consistent with similar metal complexes described by Nakamoto [52]. The spectra of complexes of the less common ligands ($Ga(detc)_3$, $Ga(2\text{-Sox})_3$, $Ga(plc)_3 \cdot H_2O$, $Ga(6\text{-Mepic})_3$ and $GaCl(2\text{-Mesx})_2$) are given in Figure 2. The yields in all syntheses were nearly stoichiometric.

Table 2A Analytic data for the compounds synthesized

Compound	% C Calc	% C Found	%H Calc	%H Found	%N Calcd	%N Found
$Ga(acac)_3$	49.08	48.54	5.76	5.49		
$In(acac)_3$	43.72	43.51	5.14	5.01		
$Ga(ttfacac)_3$	39.32	39.25	1.65	1.62		
$In(ttfacac)_3$	37.23	37.15	1.12	1.47		
$Ga(tfacac)_3$	34.06	33.34	2.29	2.80		
$Ga(\phi acac)_3$	65.13	65.93	4.92	4.85		
$Ga(\phi_2 acac)_3$	73.09	72.27	4.50	4.41		
$Ga(tropy)_3$	58.24	56.66	3.49	3.28		
$Ga(detc)_3$	35.04	35.87	5.88	5.91	8.16	8.14
$Ga(2\text{-}Sox)_3$	40.23	39.14	2.70	2.83	9.36	8.93
$Ga(pic)_3 \cdot H_2O$	47.51	47.35	3.72	3.40	9.19	8.90
$Ga(6\text{-}Mepic)_3$	52.76	51.91	3.79	3.95	8.78	8.04
$Al(2\text{-}Meox)_3$	71.85	71.39	4.82	4.87	8.37	8.08
$Ga(2\text{-}Meox)_3$	66.21	66.05	4.45	4.05	7.71	7.61
$In(2\text{-}Meox)_3$	61.14	60.58	4.10	4.03	7.13	6.82
$GaCl(2\text{-}Meox)_2$	56.99	57.11	3.83	3.66	6.44	6.70

Table 20 Melting points, calculated molecular weights and observed parent ions for compounds synthesized.

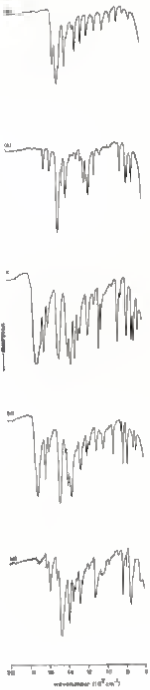
Compound	MP (°C)	MW (amu)	P^+ (m/e)
$Ga(acac)_3$	194-195	367.05	366
$In(acac)_3$	183-184	412.15	412
$Ga(ttfacac)_3$	180-182	733.27	732
$In(ttfacac)_3$	143	778.37	778
$Ga(tfacac)_3$	120-121	528.98	520
$Ga(\phi acac)_3$	210-214	553.27	*
$Ga(\phi_2 acac)_3$	276-278	739.48	*
$Ga(tr\phi p)_3$	>360	433.07	432
$Ga(dtc)_3$	239-240	514.51	*
$Ga(2\text{-}Sam)_3$	270-271	448.17	447
$Ga(plc)_3 \cdot H_2O$	332-333	434.03	435
$Ga(6\text{-}Mepic)_3$	293-294	478.09	477
$Al(ox)_3$	>400	459.42	459
$Ga(ox)_3$	>360	502.16	501
$In(ox)_3$	>360	547.16	547
$Al(2\text{-}Meox)_3$	>360	501.50	501
$Ga(2\text{-}Meox)_3$	269-270	544.24	543
$In(2\text{-}Meox)_3$	340-341	589.34	589
$GaCl(2\text{-}Meox)_2$	312	421.52	420

* P^+ not observed

Table 3: Nmr (^1H) spectra of chloroform soluble compounds synthesized

Compound	δ	Multiplicity	Area
$Ga(acac)_3$	2.00	singlet	6
	5.43	singlet	1
$In(acac)_3$	2.00	singlet	6
	5.36	singlet	1
$Ga(ttfacac)_3$	6.37	singlet	1
	7.10	multiplet	3
	7.72	multiplet	
$In(ttfacac)_3$	6.36	singlet	3
	7.14	multiplet	3
	7.73	multiplet	
$Ga(tfacac)_3$	2.25	singlet	3
	5.93	singlet	1
$Ga(\phi acac)_3$	2.14	singlet	3
	6.13	singlet	1
	7.36	multiplet	5
	7.84	multiplet	
$Ga(\phi_2acac)_3$	6.80	singlet	1
	7.37	multiplet	5
	7.95	multiplet	
$Ga(tmp)_3$	8.2	multiplet	
$GaCl(2\text{-}Meox)_2$	3.18	singlet	3
	7.22	multiplet	5

Figure 2. The Infrared spectra from 2000 to 800 cm^{-1} of (a), $Ga(dtc)_3$; (b), $Ga(2\text{-Sox})_3$, (c), $Ga(pic)_3 \cdot H_2O$, (d) $Ga(6\text{-Mepic})_3$, and (e) $GaCl(2\text{-Meox})_2$.



CHAPTER 3

DIFFRACTION EXPERIMENTAL

General Experiment

The following general description applies to all structure solutions, except where explicitly noted to the contrary in the individual experimental sections.

Preliminary space group and cell constant data were determined from Weissenberg and/or precession photographs.[53,54] For intensity measurements, accurate cell constants and the orientation matrix were obtained from a least-squares fitting of 2θ, ω, χ, and φ for approximately fifteen intense reflections centred on a Syntex P$\bar{1}$ diffractometer. All measurements were made at ambient temperature. Estimated standard deviations for the cell constants were derived from the variance-covariance matrix.

The densities of the crystals were determined by flotation in a suitable liquid, followed by the measurements of the densities of the liquids with a hydrometer. The accuracy of these measurements was $\pm 0.01 g cm^{-3}$.

The suitability of a crystal for data collection was determined by the appearance of its rotation picture, the ease with which reflections were centred, the values of the cell constants and their estimated standard deviations.

Intensities were measured with a Syntex P$\bar{1}$ diffractometer employing a variable speed θ-2θ scan technique where all the independent reflections

up to a limit $2\theta_{max}$ were measured. The scan rate depends upon the magnitude of a preliminary three-second scan of the reflection. The speed varies linearly from 1°/minute for 150 counts or less to 24°/minute for 1500 counts or more. The scan range was from 1° below the α_1 peak to 1° above the α_2 peak. background counts were taken at the end of the range. The intensity, I, was equal to:

$$I = \text{scan rate}\left[\text{total scan counts} - \frac{(\text{background counts})}{(\text{background to scan ratio})}\right]$$

with estimated standard deviation, $\sigma(I)$, of:

$$\sigma(I) = \left[\text{total scan counts} + \frac{(\text{background count})^2}{(\text{background to scan ratio})}\right]^{1/2}$$

The incident beam was monochromatized with a graphite monochromator for molybdenum radiation or 0.35mil Ni foil for copper. The stability of the system was monitored by measuring four standard reflections every 96 measurements.

The data were scaled to compensate for any fluctuations in the standard reflections, (usually ~6% overall) and averaged according to crystal class symmetry. The observed reflections were those where $I > k\sigma(I)$, where k is given in Table 5. To all reflections, Lorentz-Polarization corrections of the form

$$1/LP = \sin 2\theta/(1 + \cos^2 2\theta)$$

were then applied. For molybdenum radiation, a further correction was applied for the monochromator, assuming it was 50% perfect crystal, and 50% mosaic. The unobserved reflections were flagged with a minus sign, assigned a value of $\frac{1}{2}\sigma(I)$, and excluded from subsequent steps in the structure solution.

Overall scale and temperature factors were estimated from a Wilson plot.[55] Intensity statistics[56] were calculated in order to help choose between centric and acentric space groups where necessary. Scattering factors were obtained from Hanson, Herman, Lea and Skillman[57] and are uncorrected for the real and imaginary parts of the anomalous dispersion, except thallium, which was corrected for the real part of the anomalous dispersion.[58]

The heavy atom or atoms were located, where necessary, by means of a Patterson function[59]

$$P(UVW) = \frac{2}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F(hkl)|^2 \cos 2\pi(hU+kV+lW)$$

Once the heavy atom or atoms were located, the phase of the reflection, $\alpha(hkl)$, could be determined by the heavy atom approximation. Fourier syntheses of the form

$$\rho(xyz) = \frac{2}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F(hkl)| \cos 2\pi[(hx+ky+lz)-\alpha(hkl)]$$

were calculated and allowed the determination of other atomic positions. By using these positions and that of the heavy atom in subsequent phase determination and Fourier synthesis, further positions could be determined iteratively, by this means, all non-hydrogen positions in the asymmetric unit could be located.

The observed structure factors, on a relative scale, were placed on an absolute scale by an overall scale factor chosen to make the sum of F_{obs} equal to the sum of F_{calc}. The model was then refined by least-squares, minimizing the function

$$\text{Residual} = \Sigma\omega(||F_{obs}|-|F_{calc}||)^2$$

with the following weighting scheme.

$$\sqrt{\omega} = F_{obs}/A \qquad \text{for } F_{obs} < A$$

$$\sqrt{\omega} = 1.0 \qquad \text{for } A \leq F_{obs} \leq B$$

$$\sqrt{\omega} = B/F_{obs} \qquad \text{for } F_{obs} > B$$

where A and B are constants given in Table 4A, and using isotropic then, finally, anisotropic temperature factors. The latter has the form:

$$\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl))$$

The reliability index, R, is:

$$R = \Sigma \frac{||F_{obs}|-|F_{calc}||}{\Sigma|F_{obs}|}$$

All calculations were carried out on an IBM 370/165 computer with programs written or modified by Dr. G. J. Palenik. More specific forms of the functions used can be found in International Tables for X-ray Crystallography.[58] Specific constants for the structures solved in this work can be found in Table 4A. Table 4B contains space group and all constant data for those compounds on which preliminary crystallographic data were obtained.

Table 4A. Crystallographic and experimental data for the structures solved in this work. * denotes an angle of 90° fixed by symmetry; ** the density was not measured due to the lack of a hydrometer which would measure densities this high.

Compound	Formula	MW(gmole^{-1})	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	U(Å^3)
$Ga(acac)_3$	$C_{15}H_{21}O_6Ga$	367.05	14.003(4)	7.588(2)	16.491(3)	*	99.00(2)	*	1720.2(7)
$In(acac)_3$	$C_{15}H_{21}O_6In$	412.13	15.576(4)	13.724(5)	16.855(5)	*	*	*	3603(2)
$Ga(tcfacac)_3$	$C_{24}H_{12}O_6F_9S_3Ga$	733.27	13.375(4)	14.503(5)	14.379(3)	*	94.34(2)	*	2856(1)
$Ga(dtc)_3$	$C_{15}H_{30}N_3S_6Ga$	514.51	14.862(3)	10.250(2)	17.172(3)	*	112.64(1)	*	2414.2(8)
$Ga(pic)_3 \cdot H_2O$	$C_{18}H_{14}N_3O_7Ga$	454.03	30.087(8)	8.548(2)	13.972(6)	*	95.22(2)	*	3578(1)
$Ga(6\text{-Mapic})_3$	$C_{21}H_{18}N_3O_6Ga$	478.09	31.102(11)	8.318(4)	15.395(4)	*	92.13(3)	*	3980(3)
$InCl^R_3 \cdot tarpy$	$C_{15}H_{11}N_3Cl_3In$	454.45	8.582(1)	14.155(4)	14.360(3)	*	109.32(1)	*	1646.2(7)
$TlCl_2 \cdot tarpy$	$C_{15}H_{11}N_3Cl_3Tl$	543.98	8.637(1)	14.198(3)	14.430(3)	*	108.63(1)	*	1676.8(6)
$[GaMeMe^*dpmaCl(OH)]Cl_2 \cdot H_2O$	$C_{28}H_{36}N_8O_3Cl_4Ga_2$	785.85	13.040(7)	12.284(7)	11.000(7)	95.28(2)	84.54(3)	97.82(3)	1732.2(8)
$GaCl(Zimesx)_2$	$C_{20}H_{19}N_2O_2ClGa$	421.52	25.232(11)	9.555(2)	15.165(4)	*	93.04(3)	*	3651(2)

Table 4A, continued . . . .

Compound	D_m (g-cm^{-3})	D_c (g-cm^{-3})	Z	Systematic Extinctions	Space Group	Wilson Distribution	Crystal Size (MM)
$Ga(acac)_3$	1.41	1.417	4	hol l=2n+1 oko k=2n+1	$P2_1/c$	centric	0.28x0.23x0.11
$In(acac)_3$	1.52	1.521	8	okl k=2n+1 hol l=2n+1 hko h=2n+1	Pbca	centric	0.17x0.13x0.09
$Ga(ttfacac)_3$	1.70	1.705	4	hol h+l=2n+1 oko k=2n+1	$P2_1/n$	centric	0.18x0.17x0.04
$Ga(detc)_3$	1.38	1.383	4	hkl h+k+l=2n+1 hol h=2n+1	$I4_1/2/a$	centric	0.09x0.07x0.02
$Ga(pic)_3 \cdot H_2O$	1.69	1.687	8	hkl h+k=2n+1 hol l=2n+1	Cc,C2/c	centric	0.31x0.14x0.08
$Ga(6\text{-Mapic})_3$	1.59	1.597	8	hkl h+k=2n+1 hol l=2n+1	Cc,C2/c	centric	0.31x0.18x0.15
$InCl_3$-terpy	1.83	1.834	4	hol l=2n+1 oko k=2n+1	$P2_1/c$	centric	0.18x0.17x0.16
$TiCl_3$-terpy	**	2.157	4	hol l=2n+1 oko k=2n+1	$P2_1/c$	centric	0.17x0.14x0.09
$[GaMeMe'dmmaCl(OH)]Cl_2 \cdot H_2O$	1.55	1.500	2	none	P1,P$\bar{1}$	centric	0.17x0.11x0.06
$GaCl_2(2Meox)_2$	1.53	1.535	8	hkl h+k+l=2n+1 hol h+2n+1	$Ia,I2/a$	centric	0.47x0.22x0.20

Table 4A, continued

Compound	Radiation	$\mu(cm^{-1})$	$2\theta_{max}(°)$	# measured reflections	# observed reflections	k (kG)	Final R	A	B
$Ga(acac)_3$	Cu	25.7	110	2153	1872	1.25	0.060	12.0	48.0
$In(acac)_3$	Mo	13.3	45	2370	1516	2.00	0.038	54.0	162.0
$Ga(ttfacac)_3$	Cu	43.1	105	3257	2333	1.40	0.086	20.0	80.0
$Ga(datc)_3$	Cu	63.3	110	1310	1296	1.60	0.073	18.7	37.2
$Ga(plc)_3 \cdot H_2O$	Cu	27.2	110	2255	2035	2.00	0.052	26.5	53.1
$Ga(6\text{-}Mepic)_3$	Mo	15.1	45	2615	1730	2.00	0.047	30.0	60.0
$InCl_3 \cdot terpy$	Mo	19.1	47.5	2525	2101	2.00	0.027	32.0	64.0
$TlCl_2 \cdot terpy$	Mo	101.6	45	2211	1652	2.00	0.038	67.0	134.0
$[CaMeMe'dpmaCl(OH)]Cl_2 \cdot H_2O$	Mo	19.8	45	6152	3161	1.30	0.070	27.1	81.0
$GaCl(2Mmox)_2$	Mo	17.5	45	2408	1839	1.60	0.047	20.4	40.8

Table 4g. Preliminary space group and cell constant data for those compounds whose structures [illegible]

Compound	$Ga(trop)_3$	$In(ttfacac)_3$	$InBr_3$ MeMe^{t}dpm	$Ga(tfac[illegible])_3$
Formula	$C_{21}H_{15}O_6Ga$	$C_{21}H_{12}O_6F_9S_3In$	$C_{14}H_{16}N_3Br_3In$	$C_{15}H_{12}F_9Ga$
MW(gmole^{-1})	433.07	778.37	580.83	432.98
a(Å)	18.16	14.41	8.37	13.76
b(Å)	10.29	18.74	17.45	20.15
c(Å)	14.46	11.83	22.70	14.84
α(°)	*	*	*	*
β(°)	*	115.0	*	*
γ(°)	*	*	*	*
U(Å^3)	2702	2895	3552	4114
D_m(g-cm^{-3})	**	1.78	**	1.40
D_c(g-cm^{-3})	2.13	1.787	2.17	1.397
Z	8	4	8	8
Systematic	0kl k=2n+1	hkl h+k+l=2n+1	0kl k=2n+1	0kl k=2n+1
Extinctions	h0l l=2n+1 hk0 h=2n+1		h0l l=2n+1	h0l l=2n+1 hk0 h=2n+1

Table 4B, continued

Compound	$Ga(trop)_3$	$In(trfacac)_3$	$InBr_3$ MeMe'dpma	$Ga(trfacac)_3$
Possible Space Groups	Pbca	C2/m, Cm, C2, Cc	Pbcm, $Pbc2_1$ ($Pca2_1$)	Pbca

* Denotes an angle of 90° fixed by symmetry.

** The density was not measured due to the lack of a hydrometer which would measure [illegible]

CHAPTER 4

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS(ACETYLACETONATO)GALLIUM(III) AND TRIS (ACETYLACETONATO)INDIUM(III)

Acetylacetonate complexes are one of the oldest[60] and most studied[61,62] types of coordination compounds. For trivalent metal ions, the monoanionic bidentate acetylacetonate ligand usually forms molecular species which deviate slightly from octahedral symmetry. Complexes of this type ($M(acac)_3$; M = Al,[35] Sc,[63] V,[64] Cr,[65] Mn,[66] Fe,[67,68] and Rh[69]) have been studied extensively by means of x-ray diffraction. Lingafelter and Braun[70] have shown that an excellent linear relationship exists between metal-oxygen distance and metal-ionic radius for d^0 and d^{10} ions. Therefore, from the metal-oxygen distance in $Ga(acac)_3$ and $In(acac)_3$, an estimate of the ionic radii of gallium(III) and indium(III) can be made. The dearth of structural data for gallium(III) prompted this study of the structure of $Ga(acac)_3$ in order to determine both the "normal" gallium-oxygen distance and the effective radius of gallium(III). In the course of this work, Hon and Pfluger[35] published their structural work on $Al(acac)_3$ and $Co(acac)_3$. In their discussion, they drew conclusions with regard to $Al(acac)_3$ which seem erroneous when one considers the chemistry of group IIIA and the structures of $Rh(acac)_3$[69] and $Sc(acac)_3$[63] that have been subsequently reported. As a result of these conflicts, we undertook the structure of $In(acac)_3$.

Solution of Structure of $Ga(nsac)_3$

A sharpened three-dimensional Patterson function was calculated and the position of the gallium atom determined. This was not completely unambiguous since the (2x, 2y, 2z) vector was nearly in the Harker plane. Comparison of the peak profiles for the two large vectors in the Harker plane showed that one was slightly less intense than the other. This less intense peak was assigned to the (2x, 2y, 2z) vector and a Fourier synthesis, based on the Ga atom alone, with y = 1/4, was calculated. The coordination sphere was unambiguously assigned, although a pseudo-mirror was created at y = 1/4. From a novel atom Fourier synthesis, the remaining fifteen carbon atoms were located, R = 0.21. The structure was refined with three cycles of full-matrix least-squares with individual isotropic thermal parameters, R = 0.14; followed by three cycles of full-matrix least-squares with individual anisotropic thermal parameters, R = 0.06. A difference Fourier synthesis was calculated from which no hydrogen positions could be located. Since all shifts in the last cycle of least-squares were less than one-fifth of their respective estimated standard deviations, the structure was considered solved. In order to completely resolve the ambiguity of the Patterson, a refinement was attempted on positions related by (x, y, z + 1/4). This diverged indicating our original interpretation was correct.

Results for $Ga(nsac)_3$

Final positional and thermal parameters for $Ga(nsac)_3$ are given in Table 5. Table 6 contains observed and calculated structure factors for the structure. Bond lengths and bond angles for the molecule appear in Table 7. Figure 3, an ORTEP[71] diagram of the molecule shows the atomic numbering scheme used.

Table 5 Final positional and thermal parameters ($\times 10^4$) for non-hydrogen atoms in $Ga(acac)_3$ with their respective estimated standard deviations in parentheses. The parameters of the Ga atom are $\times 10^5$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ga	26242(7)	26678(13)	2949(5)	678(5)	2335(23)	322(4)	-424(21)	132(7)	43(16)
O1	1355(4)	1894(7)	-263(3)	49(3)	236(13)	41(2)	- 47(11)	- 1(5)	- 1(9)
O2	2429(4)	5011(7)	-189(3)	82(4)	220(12)	38(3)	- 79(12)	9(5)	22(9)
O3	3201(4)	1881(8)	-649(3)	60(4)	352(16)	31(2)	- 6(12)	20(5)	4(9)
O4	3867(5)	3419(9)	888(3)	79(5)	359(17)	36(3)	-125(15)	-33(5)	26(10)
O5	2817(4)	292(7)	751(3)	80(4)	218(12)	36(2)	2(11)	17(5)	8(9)
O6	2035(4)	3465(7)	1242(3)	104(5)	208(12)	32(2)	- 2(12)	45(5)	13(9)
C1	716(6)	2530(13)	-629(5)	53(5)	293(24)	38(4)	- 20(19)	31(7)	-47(15)
C2	813(7)	4694(13)	-805(5)	69(6)	247(23)	52(4)	27(20)	17(8)	- 8(16)
C3	1665(8)	5640(12)	-604(5)	98(8)	230(20)	24(3)	17(21)	24(8)	-12(13)
C4	-277(6)	2023(15)	-931(7)	48(6)	433(33)	84(6)	- 65(22)	13(9)	-21(22)
C5	1714(8)	7515(13)	-895(6)	153(10)	175(19)	55(4)	- 15(24)	35(10)	31(16)

continued

Table 5, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C6	4067(8)	1276(20)	- 694(6)	78(7)	744(51)	37(4)	97(32)	30(9)	74(23)
C7	4817(7)	2409(30)	- 78(7)	56(7)	1286(88)	55(6)	- 82(47)	- 6(10)	102(42)
C8	4668(8)	3185(20)	676(6)	65(7)	755(52)	47(5)	-170(32)	-44(10)	125(25)
C9	4342(10)	1099(27)	-1495(7)	107(10)	1184(83)	57(6)	320(47)	58(12)	-28(36)
C10	5517(10)	3797(29)	1290(8)	106(10)	1265(95)	69(7)	-432(52)	-93(14)	172(41)
C11	2653(5)	- 222(11)	1458(5)	43(5)	222(19)	41(4)	- 52(15)	-26(7)	15(14)
C12	2261(6)	824(12)	2020(5)	72(5)	210(20)	38(4)	-12(17)	10(8)	31(14)
C13	1980(5)	2560(12)	1878(4)	58(5)	269(21)	27(3)	-55(19)	7(6)	-14(15)
C14	2905(6)	-2130(11)	1659(5)	84(6)	193(19)	54(4)	15(18)	-20(8)	50(14)
C15	1532(7)	3553(13)	2542(5)	108(8)	324(25)	41(4)	42(22)	51(9)	-18(16)

Table 5. Observed and calculated structure factors for $Ga(acac)_3$. The three columns in each group contain the values, reading from left to right, of l, $10F_{obs}$ and $10F_{calc}$. A negative F_{obs} indicates an unobserved reflection which was not included in the least-squares refinement.

Table 7. Bond lengths, non-bonded contacts and bond angles for $Ga(acac)_3$ with their estimated standard deviations in parentheses.

(a) Bond Lengths (Å)

Ga-O1	1.956(5)	O3-C6	1.254(13)
Ga-O2	1.949(5)	C6-C9	1.532(17)
Ga-O3	1.947(5)	C6-C7	1.381(17)
Ga-O4	1.941(7)	C7-C8	1.412(18)
Ga-O5	1.954(5)	C8-C10	1.506(18)
Ga-O6	1.964(6)	C8-O4	1.239(14)
O1-C1	1.267(10)	O5-C11	1.277(10)
C1-C4	1.561(13)	C11-C14	1.514(12)
C1-C2	1.381(14)	C11-C12	1.392(12)
C2-C3	1.388(14)	C12-C13	1.384(13)
C3-C5	1.505(13)	C13-C15	1.535(12)
C3-O2	1.267(11)	C13-O6	1.260(9)

(b) Non-bonded Contacts (Å)

O1-O2	2.792(8)	O2-O6	2.754(7)
O1-O3	2.755(8)	O3-O4	2.800(8)
O1-O5	2.715(8)	O3-O5	2.719(7)
O1-O6	2.769(7)	O4-O5	2.781(9)
O2-O3	2.763(8)	O4-O6	2.717(9)
O2-O4	2.742(9)	O5-O6	2.814(8)

(c) Bond Angles (°)

O1-Ga-O2	91.3(2)	C2-C3-O2	123.7(8)
O1-Ga-O3	89.8(2)	C3-O2-Ga	128.0(6)
O1-Ga-O4	177.8(2)	Ga-O3-C6	125.8(7)
O1-Ga-O5	88.0(2)	O3-C6-C7	125.6(12)
O1-Ga-O6	89.9(2)	O3-C6-C9	114.7(11)
O2-Ga-O3	90.4(2)	C9-C6-C7	119.6(12)
O2-Ga-O4	89.7(3)	C6-C7-C8	124.5(14)
O2-Ga-O5	178.5(2)	C7-C8-O4	124.8(12)
O2-Ga-O6	89.5(2)	C7-C8-C10	120.3(12)
O3-Ga-O4	92.2(3)	C10-C8-O4	115.0(11)
O3-Ga-O5	88.4(2)	C8-O4-Ga	126.7(7)
O3-Ga-O6	179.7(2)	Ga-O5-C11	126.5(5)
O4-Ga-O5	91.1(2)	O5-C11-C12	124.8(7)
O4-Ga-O6	88.2(3)	O5-C11-C14	114.9(7)
O5-Ga-O6	91.3(2)	C14-C11-C12	120.3(7)

Table 7. continued

Ga-O1-C1	124.0(5)	C14-C12-C13	124.3(8)
O1-C1-C4	114.0(7)	C12-C13-O6	127.2(8)
C4-C1-C2	115.2(8)	C12-C13-C15	119.0(7)
C1-C2-C3	124.1(9)	C15-C13-O6	113.8(7)
C2-C3-C5	115.6(8)	C13-O6-Ga	125.0(5)
C5-C3-O2	116.7(8)		

TABLE 8 Least-squares planes for $Ga(acac)_3$ in orthogonal coordinates The title and equation of the plane are given, followed by the atoms with their deviations ($\times 10^3$) from the plane (in Å) in parentheses The atoms used to define the plane are noted by an asterisk following the deviation

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I Ligand Backbone (O1, O2, C1, C2, C3)
$-0.4349X + 0.2437Y + 0.8667Z = -0.8579$
Ga(200), O1(-14)*, O2(20)*, C1(11)*, C2(11)*, C3(-28)*, C4(-3), C5(-153)

II Ligand Backbone (O3, O4, C6, C7, C8)
$0.0104X + 0.9077Y - 0.4195Z = 1.7992$
Co(-125), O3(-15)*, O4(6)*, C6(25)*, C7(-17)*, C8(1)*, C9(40), C10(16)

III Ligand Backbone (O5, O6, C11, C12, C13)
$0.8631X + 0.3018Y + 0.4048Z = 3.7944$
Ga(117), O5(3)*, O6(-2)*, C11(-5)*, C12(3)*, C13(0)*, C14(-52), C15(-26)

IV Plane Through Ga, O1, O2
$-0.5411X + 0.3001Y + 0.7856Z = -0.9649$
Ga(0)*, O1(0)*, O2(0)*

V Plane Through Ga, O3, O4
$-0.0786X + 0.9090Y - 0.4092 = 1.3618$
Ga(0)*, O3(0)*, O4(0)*

VI Plane Through Ga, O5,O6
$0.8371X + 0.2667Y + 0.4776Z = 3.7808$
Ga(0)*, O5(0)*, O6(0)*

Dihedral angles between planes I-IV, II-V and III-VI are 8°20', 5°8' and 4°52' respectively.

Solutions of Structure of $In(acac)_3$

Tris acetyacetonate complexes of trivalent metal ions fall into two distinct crystal classes. The monoclinic modification includes $Cr(acac)_3$,[65] $Co(acac)_3$[35] and a polymorph of $Al(acac)_3$,[35] $Ga(acac)_3$, $In(acac)_3$ and $Mn(acac)_3$.[66] $Fe(acac)_3$,[67] $Sc(acac)_3$[63] and a polymorph of $Ga(acac)_3$, $In(acac)_3$, $V(acac)_3$[64] and $Mn(acac)_3$[66] crystallize in an orthorhombic modification.

Comparison of several large observed structure factors for $Fe(acac)_3$[67] and $In(acac)_3$ showed that they were related by a constant proportionality factor. We concluded that the two structures were isomorphous and calculated a Fourier synthesis for $In(acac)_3$ based on the final fractional coordinates for all non-hydrogen atoms of the $Fe(acac)_3$ structure.[68] R = 0.14. The $In(acac)_3$ structure was refined with three full-matrix least-squares cycles with individual isotropic thermal parameters, R = 0.060. Three full-matrix least-squares cycles with individual anisotropic thermal parameters refined the structure to R = 0.042. A difference Fourier synthesis was calculated and all hydrogen positions were located. Three block-diagonal least-squares cycles, with individual anisotropic thermal parameters for non-hydrogen atoms and individual isotropic thermal parameters for the hydrogen atoms, refined the structure to R = 0.034. All shifts for non-hydrogen atom parameters were less than one-tenth of their respective estimated standard deviations; the refinement was considered complete.

Results for $In(acac)_3$

Final positional and thermal parameters for $In(acac)_3$ are given in Table 9. Calculated and observed structure factors are found in

Table 9 Final positional and thermal parameters ($x10^4$) for non-hydrogen atoms in $In(acac)_3$ with their respective estimated standard deviations in parentheses. The parameters of the In atom are $x10^5$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
In	14259(3)	26891(3)	24244(3)	444(2)	514(2)	344(2)	121(5)	8(6)	- 7(5)
O1	711(4)	3578(4)	3224(3)	72(3)	60(3)	46(2)	13(6)	16(5)	-40(5)
O2	376(3)	1690(3)	2505(4)	42(2)	61(3)	76(3)	- 7(4)	5(7)	-23(8)
O3	921(3)	3420(4)	1413(3)	69(3)	81(4)	40(2)	57(6)	-29(4)	- 5(5)
O4	2025(3)	1736(4)	1585(3)	71(3)	69(4)	43(2)	40(6)	15(4)	-10(5)
O5	2439(3)	3730(3)	2503(4)	59(2)	54(3)	62(2)	- 3(4)	-13(7)	25(7)
O6	2078(3)	1915(4)	3331(3)	54(3)	68(3)	47(2)	- 8(5)	-25(4)	37(5)
C1	- 24(5)	3393(6)	3513(4)	67(5)	72(6)	36(3)	41(9)	27(7)	- 1(7)
C2	-512(5)	2553(6)	3387(5)	65(5)	69(6)	40(4)	28(10)	36(7)	6(8)
C3	-303(5)	1776(5)	2915(4)	41(4)	65(5)	55(4)	22(8)	-15(6)	23(7)
C4	-350(7)	4170(8)	4041(6)	117(9)	111(8)	71(5)	36(14)	71(11)	-69(11)
C5	-896(5)	903(6)	2873(6)	42(4)	75(6)	102(6)	-13(8)	5(8)	26(9)

continued . . . .

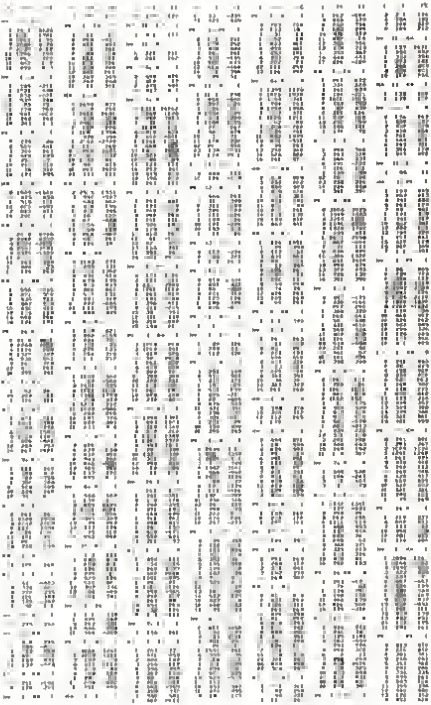
Table 9, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C6	967(5)	3178(6)	698(5)	60(5)	75(6)	45(3)	- 8(9)	-32(7)	20(7)
C7	1407(6)	2355(6)	412(4)	93(5)	89(6)	39(3)	15(12)	-24(8)	-15(8)
C8	1897(5)	1712(6)	847(4)	64(5)	63(6)	45(3)	- 9(9)	28(7)	-45(7)
C9	518(7)	3825(8)	117(5)	131(8)	130(9)	52(5)	92(15)	-47(11)	46(10)
C10	2379(7)	508(7)	418(5)	109(7)	95(8)	65(5)	48(12)	32(11)	-64(10)
C11	3080(5)	3709(5)	2961(5)	51(4)	57(5)	59(4)	22(8)	1(7)	-23(7)
C12	3282(5)	2960(6)	3471(5)	52(5)	74(6)	62(4)	- 8(8)	-33(7)	2(8)
C13	2797(5)	2131(6)	3611(4)	75(5)	83(7)	39(3)	44(9)	-19(7)	31(8)
C14	3668(6)	4592(6)	2908(6)	66(5)	68(5)	104(6)	-40(10)	2(9)	-29(9)
C15	3188(7)	1354(8)	4196(6)	113(8)	142(10)	93(6)	34(15)	-80(12)	141(13)

Table 10 Final refined parameters for the hydrogen atoms in $In(acac)_3$. The hydrogen atom is given followed by the atom to which it is bonded. The corresponding bond distances (in Å), the positional parameters ($\times 10^3$) and the isotropic thermal parameter (in $Å^2$) follow.

Atom	Bonded to	Distance	x	y	z	B
H2	C2	0.94	-103	266	367	8.8
H4	C4	0.76	- 9	418	444	15.9
H4'	C4	1.10	-100	409	432	11.2
H4"	C4	0.92	- 45	478	386	15.3
H5	C5	0.88	- 90	67	239	11.2
H5'	C5	1.08	- 68	39	331	8.8
H5"	C5	0.95	-145	108	306	7.0
H7	C7	1.01	147	204	- 13	10.9
H9	C9	0.73	86	385	- 17	12.8
H9'	C9	1.09	37	370	- 51	18.6
H9"	C9	0.92	15	426	35	11.4
H10	C10	0.85	212	81	- 2	10.0
H10'	C10	1.02	274	71	90	22.3
H10"	C10	0.92	222	35	67	8.6
H12	C12	1.19	393	316	381	13.7
H14	C14	0.94	426	447	297	12.2
H14'	C14	0.97	364	490	343	11.2
H14"	C14	0.80	343	489	257	12.0
H15	C15	0.66	308	173	397	9.3
H15'	C15	0.96	337	151	473	14.6
H15"	C15	0.90	283	85	431	17.8

Table 11. Observed and calculated structure factors for $In(acac)_3$. The three columns in each group contain the values, reading from left to right, of l, $10F_{obs}$ and $10F_{calc}$. The unobserved reflections were not included.



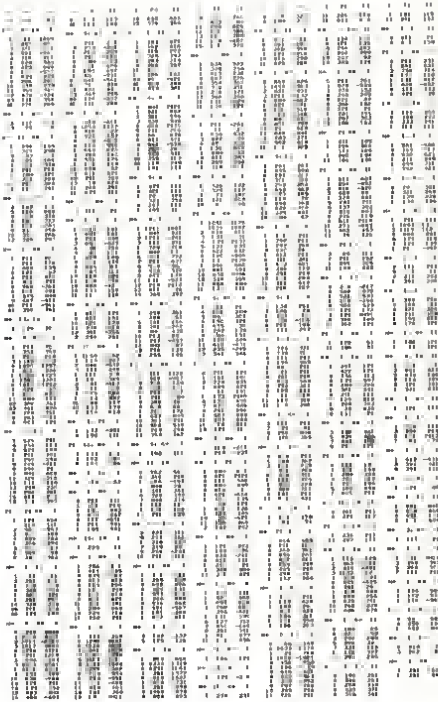


Table 12. Bond lengths, non-bonded contacts and bond angles for $In(acac)_3$ with their estimated standard deviations in parentheses.

(a) Bond Lengths (Å)

In-O1	2.132(5)	O3-C6	1.252(9)
In-O2	2.138(4)	C4-C9	1.495(13)
In-O3	2.130(5)	C6-C7	1.406(12)
In-O4	2.141(5)	C7-C8	1.379(11)
In-O5	2.133(4)	C8-C10	1.517(13)
In-O6	2.118(5)	C8-O4	1.260(9)
O1-C1	1.270(10)	O5-C11	1.263(9)
C1-C4	1.499(13)	C11-C14	1.522(11)
C1-C2	1.397(12)	C11-C12	1.375(11)
C2-C3	1.370(11)	C12-C13	1.386(11)
C3-C5	1.514(11)	C13-C15	1.575(14)
C3-O2	1.269(9)	C13-O6	1.254(9)

(b) Non-bonded Contacts (Å)

O1-O2	2.908(7)	O2-O4	3.008(7)
O1-O3	3.079(7)	O3-O4	2.895(7)
O1-O5	2.960(7)	O3-O5	3.025(7)
O1-O6	3.125(7)	O4-O5	3.209(7)
O2-O3	3.122(7)	O4-O6	2.954(7)
O2-O4	3.000(7)	O5-O6	2.911(7)

(c) Bond Angles (°)

O1-In-O2	85.9(2)	C5-C3-O2	114.2(6)
O1-In-O3	92.5(2)	C2-C3-O2	125.8(7)
O1-In-O4	174.3(2)	C3-O2-In	127.8(5)
O1-In-O5	87.9(2)	In-O3-C6	128.6(5)
O1-In-O6	94.6(2)	O3-C6-C7	124.9(7)
O2-In-O3	94.0(2)	O3-C6-C9	116.4(7)
O2-In-O4	89.1(2)	C9-C6-C7	118.7(8)
O2-In-O5	172.5(2)	C6-C7-C8	127.0(8)
O2-In-O6	89.9(2)	C7-C8-O4	126.6(7)
O3-In-O4	85.4(2)	C7-C8-C10	119.1(7)
O3-In-O5	90.4(2)	C10-C8-O4	114.3(7)
O3-In-O6	172.1(2)	C8-O4-In	126.9(5)
O4-In-O5	97.4(2)	In-O5-C11	127.4(5)
O4-In-O6	87.8(2)	O5-C11-C12	125.5(7)
O5-In-O6	86.4(2)	O5-C11-C14	114.8(7)
In-O1-C1	126.8(5)	C14-C11-C12	119.7(7)
O1-C1-C4	113.6(7)	C11-C12-C13	126.5(7)
C4-C1-C2	119.7(7)	C12-C13-O6	128.2(7)
C1-C2-C3	127.0(7)	C12-C13-C15	116.9(7)
C2-C3-C5	119.9(7)	C15-C13-O6	115.0(7)
		C13-O6-In	125.8(5)

Table 13. Least squares planes for $In(acac)_3$ in orthogonal coordinates. The title and equation of the plane are given, followed by the atoms with their deviations ($\times 10^3$) from the plane (in Å) in parentheses. The atoms used to define the plane are noted by an asterisk following the deviation.

I Ligand Backbone (O1, O2, C1, C2, C3)

0.4449X - 0.4472Y + 0.7760Z = 2.5056

In(3), O1(8)*, O2(-7)*, C1(-11)*, C2(2)*, C3(7)*, C4(4), C5(76)

II Ligand Backbone (O3, O4, C6, C7, C8)

0.8067X + 0.5749Y - 0.13672 = 3.5421

In(-187), O3(-12)*, O4(7)*, C6(19)*, C7(-11)*, C8(-3)*, C9(99), C10(67)

III Ligand Backbone (O5, O6, C11, C12, C13)

0.4835X - 0.4933Y - 0.7231Z =-3.7661

In(65), O5(27)*, O6(-26)*, C11(-34)*, C12(4)*, C13(29)*, C14(-125), C15(137)

IV Plane Through In, O1, O2

0.4427X - 0.4518Y + 0.7715Z = 2.4804

In(0)*, O1(0)*, O2(0)*

V Plane Through In, O3, O4

0.8034X + 0.5951Y - 0.0205Z = 3.8968

In(0)*, O3(0)*, O4(0)*

VI Plane Through In, O5, O6

0.5151X + 0.5048Y - 0.6928Z = -3.5437

In(0)*, O5(0)*, O6(0)*

Dihedral angles between plane I-IV, II-V and III-VI are 17°, 6°46' and 2°35'.

Table 10, bond lengths and angles are listed in Table 11. Figure 4, an ORTEP[71] diagram of the molecule, shows the atomic numbering scheme used.

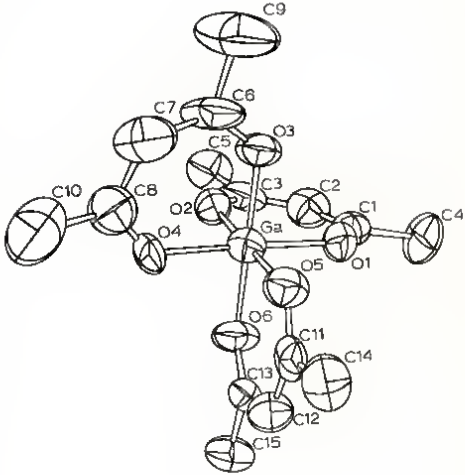
Discussion

Both $Ga(acac)_3$ and $In(acac)_3$ are octahedral molecular species with approximate D_3 symmetry. A comparison of bond angles (Tables 7,12) shows that the former complex is less distorted from exact octahedral geometry than the latter. This larger distortion may arise in $In(acac)_3$, due to the larger size of the central metal ion and the inability of the ligand bite to open to accomodate the metal. The bond lengths and angles in the ligands in both molecules agree well with those listed by Lingafelter and Braun[70] and with those structures published recently.[35,63,66] All ligands are planar within experimental error (Tables 8, 13) consistent with their delocalization.[72]

In $Ga(acac)_3$, the gallium-oxygen distance ranges from 1.941(7)Å to 1.964(6)Å, with an average value of 1.952(6)Å. This gives an effective radius of 0.56Å versus 0.62Å for the six-coordinate ionic radius.[5] In $In(acac)_3$, the indium-oxygen distances ranges from 2.118(5)Å to 2.141(5) and averages 2.132(5)Å. This yields an effective radius of 0.74Å compared with six-coordinate ionic radius of 0.79Å.[5]

Three interactions determine the equilibrium positions in the coordination sphere of these complexes. These include the metal-oxygen bonding interactions, the inter-ligand repulsions and the steric constraints of the ligand. From structural data, the magnitude of these interactions can be inferred to some degree, from metal-oxygen

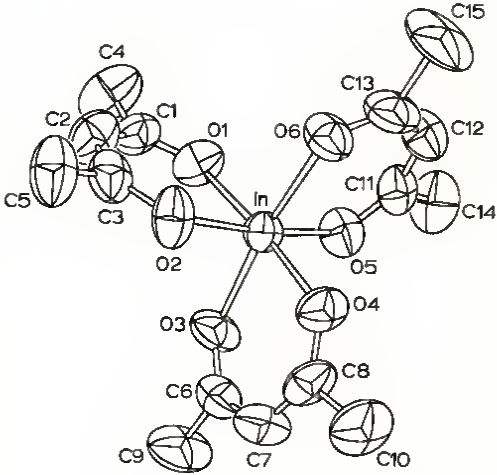
Figure 3: An ORTEP drawing of $Ga(acac)_3$ showing the atomic numbering and thermal ellipsoids.


C9
C6
C7
O3
C5
C3
C2
C10
C8
O2
C1
C4
O4
Ga
O5
O1
O6
C11
C14
C13
C12
C15

distances, non-bonded distances in the coordination sphere and ligand bite. The correlations which exist among these three parameters and with other parameters such as ionic radius may enable us to determine which factor or factors determine the final geometry of these complexes.

Attempts to correlate these properties have previously been made by Lingafelter and Braun,[70] and Hon and Pfluger.[35] The former, using all acetylacetonate data, showed that there was a linear correlation between metal-oxygen distance and metal-ionic radius. Also, a linear but poorer correlation exists between bite and ionic radius to charge ratio. Hon and Pfluger,[35] considering only trivalent metal acetylacetonate complexes, showed that there was also a linear correlation between bite and metal-oxygen distance. In light of the correlation between metal-oxygen distance and metal ionic radius, the ligand bite depends on the size of the metal ion. $Al(acac)_3$ was considered "anomalous" because it did not fit the line drawn by Hon and Pfluger (Figure 5(a)). This was rationalized on the basis of Al^{+3} having a high charge which so polarized the aluminum-oxygen bond that exceptionally large inter-ligand van der Waals forces were created, causing the ligand bite to contract. This explanation seems unsuitable because the electronegativity difference between oxygen and aluminum is small, therefore, the bond should be more covalent and less polarized than other acetylacetonate complexes. Furthermore, if one assumes that the acidity of a metal's hexaaqua ion reflects ionic character in the metal-oxygen bond, then $Ga(acac)_3$ should be as anomalous as $Al(acac)_3$, since the K_a's for $Al(H_2O)_6^{+3}$ and $Ga(H_2O)_6^{+3}$ are 1.12×10^{-5} and 3.5×10^{-3} respectively.[73] Clearly, from Figure 5(a), Ga is not anomalous.

Figure 4. An ORTEP drawing of $In(acac)_3$ showing the atomic numbering and thermal ellipsoids.

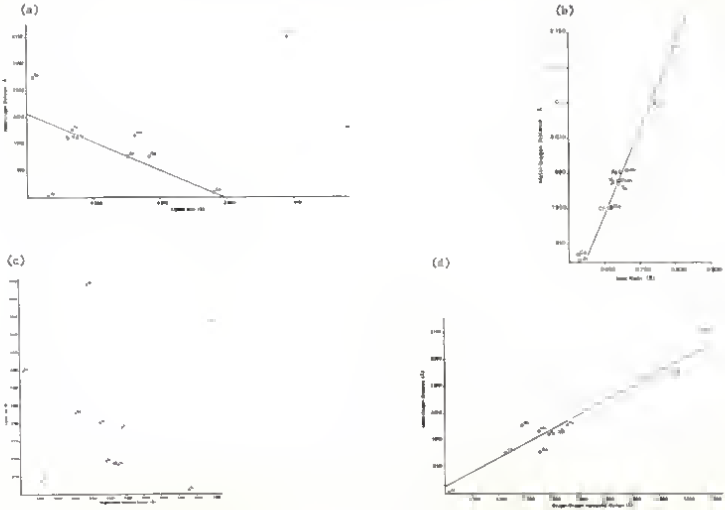

C15
C4
C13
C2
C1
O1
O6
C12
C5
C11
In
C14
C3
O2
O5
O4
O3
C8
C6
C9
C7
C10

With $Ga(acac)_3$, $Sr(acac)_3$, $Rh(acac)_3$, $In(acac)_3$ and the correct $Mn(acac)_3$ structural data, we can obtain an excellent correlation between metal-oxygen distance and metal-ionic radius (Figure 5(b)). With metal-oxygen distance and ligand bite (Figure 5(a)), no overall trend exists, although, in individual periods, a trend may be observed. This, therefore, implies that metal size does not control ligand bite.

There is no correlation either between ligand bite and oxygen-oxygen non-bonded contact (Figure 5(c)). Therefore, van der Waals forces do not control ligand bite. The non-bonded contacts, however, do correlate linearly with the metal-oxygen distance (Figure 5(d)). As a result, the magnitude of the inter-ligand van der Waals interaction depends roughly on the metal size.

What, then, does affect ligand bite? Likely all the above factors contribute. However, the metal-ligand bonding interactions cannot simply be represented by distances because, by just taking size into account, we neglect the covalent character of the metal-oxygen bond. This covalent character is extremely important for it may allow a great deal of distortion in the ligand.

Figure 5. Correlations of structural parameters of tris, acetylacetonate complexes of trivalent metals. Plots of (a), metal-oxygen distance versus ligand bite, (b) metal-oxygen distance versus metal-ionic radius, (c) ligand bite versus oxygen-oxygen non-bonded contact, (d) metal-oxygen distance versus oxygen-oxygen non-bonded contact.


(a)
(b)
(c)
(d)

CHAPTER 5

A CIS EFFECT: THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS(THIENYLTRIFLUOROACETYLACETONATO) GALLIUM(III)

In the evaluation of structural parameters, one must consider both electronic and steric factors. In general, it is usually impossible to evaluate both independently. In order to minimize steric effects and evaluate electronic parameters in the gallium(III) system, we wished to compare the structures of $Ga(tfacac)_3$ and $Ga(acac)_3$, since steric factors in acac and tfacac are very similar. Unfortunately, the crystals of $Ga(tfacac)_3$ were unsuitable for intensity measurements. Therefore, the structure of $Ga(ttfacac)_3$ was undertaken. The steric constraints of ttfacac and acac are quite different and must be considered as well as the electronic effects of the asymmetric ttfacac.

Solution of Structure of $Ga(ttfacac)_3$

A sharpened three-dimensional Patterson function was calculated from which the position of the Ga atom was determined. The positions of the three sulphur atoms were located from a Fourier synthesis which was phased on the Ga atom. Subsequent Fourier syntheses enabled us to establish all the non-hydrogen atom positions, R was 0.21. Three full-matrix least-squares cycles with individual isotropic thermal parameters refined the model to R = 0.15. Six block-diagonal least-squares cycles with individual anisotropic thermal parameters refined the model further, R = 0.09. A difference Fourier synthesis was calculated and the positions

Table 14 Final positional and thermal parameters ($\times 10^{+4}$) for non-hydrogen atoms in $Ga(ttfacac)_3$ with their respective estimated standard deviations in parentheses. The parameters of the Ga atom are $\times 10^{+5}$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ga	1907(1)	1987(1)	625(1)	80(1)	53(1)	63(1)	− 32(2)	2(1)	− 10(1)
S11	3536(3)	2955(3)	3438(3)	97(3)	86(2)	89(3)	− 20(5)	−26(4)	− 17(5)
S21	3973(3)	−644(3)	1123(3)	105(3)	64(2)	121(3)	− 24(4)	−29(5)	46(4)
S31	− 562(3)	4135(3)	1390(3)	92(3)	75(2)	98(3)	− 26(4)	25(4)	− 3(4)
O11	2432(5)	2154(5)	1921(5)	81(5)	71(5)	61(5)	− 44(9)	− 3(8)	− 18(8)
O12	841(5)	1258(5)	997(5)	82(5)	56(5)	52(4)	− 51(8)	− 9(8)	5(7)
O21	2720(5)	875(4)	563(5)	81(6)	41(4)	70(5)	8(8)	− 4(8)	− 4(7)
O22	1524(5)	1900(5)	−701(5)	87(5)	48(4)	54(4)	− 14(8)	−16(8)	− 7(7)
O31	1055(5)	3064(5)	772(5)	70(5)	43(4)	73(5)	− 24(8)	10(8)	− 8(8)
O32	2947(5)	2787(5)	300(5)	81(5)	50(4)	84(5)	− 29(8)	25(8)	− 13(7)
F11	− 334(8)	− 96(7)	1327(8)	185(10)	147(8)	187(10)	−228(15)	131(16)	−113(15)
F12	−1025(6)	1004(7)	1793(10)	78(6)	140(8)	328(16)	− 20(12)	3(15)	174(19)
F13	− 305(7)	161(7)	2708(6)	180(9)	173(9)	113(7)	−197(16)	−37(13)	105(13)

Table 14, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
F21	2257(7)	2589(6)	-2373(6)	190(9)	130(7)	83(6)	-143(13)	- 8(11)	70(10)
F22	2129(6)	1230(6)	-2888(5)	162(8)	136(7)	64(5)	102(13)	4(10)	-11(9)
F23	307(5)	1938(5)	-2478(5)	105(6)	108(6)	79(5)	29(10)	-23(8)	12(9)
F31	4209(8)	3796(7)	- 564(8)	199(10)	148(8)	173(9)	-194(16)	209(17)	-97(15)
F32	3929(6)	4969(6)	228(9)	102(7)	70(5)	326(15)	- 52(10)	162(16)	-29(14)
F33	4638(7)	3844(7)	745(9)	110(7)	150(9)	232(12)	- 86(13)	-19(15)	61(16)
C11	2042(8)	1938(8)	2651(8)	79(8)	49(6)	75(8)	16(13)	-29(13)	31(13)
C12	1168(8)	1393(8)	2674(8)	76(9)	57(7)	80(9)	5(13)	15(14)	4(13)
C13	664(8)	1118(7)	1817(8)	74(8)	35(6)	83(8)	- 25(12)	-12(13)	12(12)
C14	-262(10)	577(10)	1960(9)	116(12)	86(10)	66(8)	- 53(17)	- 4(16)	40(15)
C15	2504(8)	2258(7)	3539(7)	66(8)	61(7)	57(7)	68(12)	-54(12)	-25(11)
C16	2310(8)	2125(7)	4447(8)	75(8)	54(7)	67(7)	59(13)	-24(12)	- 4(12)
C17	3014(10)	2607(9)	5048(9)	104(11)	92(9)	71(9)	59(17)	-48(16)	-22(15)
C18	3688(10)	3030(10)	4573(10)	90(10)	97(10)	100(10)	7(17)	-66(16)	-61(18)

Table 14, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C21	2997(8)	493(7)	- 159(8)	60(8)	39(6)	85(8)	-29(11)	10(12)	-20(11)
C22	2738(8)	801(8)	-1076(8)	70(8)	54(7)	67(8)	- 7(12)	-16(12)	-23(12)
C23	2041(8)	1453(7)	-1265(8)	74(8)	41(6)	64(7)	-51(12)	3(12)	-27(11)
C24	1821(9)	1805(9)	-2265(9)	91(9)	84(9)	84(9)	- 5(16)	24(15)	0(15)
C25	3633(8)	- 303(8)	3(9)	73(9)	46(7)	106(10)	-53(13)	- 9(15)	14(13)
C26	4077(8)	-863(7)	- 695(9)	60(8)	43(6)	104(10)	2(12)	11(14)	21(13)
C27	4698(10)	-1501(10)	- 213(12)	97(11)	74(10)	149(14)	-40(17)	18(20)	- 1(19)
C28	4714(9)	-1513(8)	723(11)	77(10)	49(7)	167(13)	-27(14)	10(19)	18(17)
C31	1286(8)	3909(8)	855(7)	80(8)	63(7)	46(7)	-31(13)	2(12)	10(11)
C32	2254(9)	4230(8)	676(9)	87(9)	54(7)	88(9)	-36(13)	17(15)	-18(13)
C33	2961(9)	3661(8)	426(8)	83(9)	65(8)	63(8)	-34(14)	7(13)	-14(12)
C34	3873(10)	4122(10)	174(11)	96(11)	84(10)	125(12)	-58(17)	38(19)	-65(18)
C35	370(8)	4536(8)	1131(7)	74(8)	73(8)	40(6)	17(13)	5(11)	-13(11)
C36	618(8)	5508(7)	1199(8)	72(8)	45(6)	79(8)	-30(12)	35(13)	- 6(12)

Table 14, continued .

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C37	-293(11)	5846(9)	1431(9)	140(13)	82(8)	88(10)	-22(17)	12(18)	-13(15)
C38	-975(9)	5202(9)	1586(9)	82(10)	80(9)	91(10)	15(15)	52(15)	-40(15)

Table 15. Final parameters for the hydrogen atoms in $Ga(ttfacac)_3$. The hydrogen atom is given followed by the atom to which it is bonded. The corresponding bond distance (in Å), the positional parameters ($\times 10^3$) and the isotropic thermal parameters (in $Å^2$) follows.

Atom	Bonded to	Distance	x	y	z	B
H12	C12	1.00	72	177	304	8.52
H22	C22	1.16	307	31	-161	5.72
H32	C32	1.18	240	502	82	6.41
H16	C16	0.75	203	183	476	6.28
H17	C17	1.14	313	282	581	7.75
H18	C18	1.19	447	343	469	8.44
H26	C26	1.05	408	- 89	-141	6.40
H27	C27	1.23	492	-218	- 86	8.42
H28	C28	1.39	509	-218	134	8.00
H36	C36	0.92	100	591	88	6.38
H37	C37	0.89	- 46	840	140	8.60
H38	C38	0.99	-161	537	183	7.25

Table 16 Observed and calculated structure factors for $Ga(ttfacac)_3$. The three columns in each group contain the values, reading from left to right, of l, $10F_{obs}$ and $10F_{calc}$. The unobserved reflections were not included.

of all twelve hydrogen atoms were located. The hydrogen atoms were arbitrarily assigned isotropic thermal parameters, one unit larger than those of the atoms to which they are bonded. Three block-diagonal least-squares cycles with individual anisotropic thermal parameters for non-hydrogen atoms and the hydrogen atoms held constant, refined the structure to R = 0.086. Since all shifts were now a third or less of their respective estimated standard deviations, the refinement was considered complete.

Results and Discussion

Final positional and thermal parameters for non-hydrogen atoms are given in Table 14. Table 15 contains a list of probable hydrogen positions and their respective carbon-hydrogen bond lengths. Calculated and observed structure factors for $Ga(ttfacac)_3$ are found in Table 16. An ORTEP[71] diagram of the molecule appears in Figure 6 with the atomic numbering scheme used.

$Ga(ttfacac)_3$ is a molecular octahedral species which occurs in the solid state as the meridional or trans isomer. $Ga(tfacac)_3$ also appears in the solid state as the trans isomer, but it isomerizes in solution to the facial or cis isomer.[74] The barrier to isomerization for this process is ~18Kcal/mole.[74] The steric similarity of tfacac and acac thus allow us to conclude that there is little difference in electronic effects between the cis and trans isomers of $Ga(tfacac)_3$. A study of the stability constants of $Cu(tfacac)_2$ and $Cu(ttfacac)_2$ shows that tfacac and ttfacac form equally stable copper compounds.[75] Therefore, these ligands are electronically similar and, as a result, the trans isomer of $Ga(ttfacac)_3$ should be slightly favored electronically.

Table 17. Bond lengths, non-bonded contacts and bond angles for $Ga(tcfacac)_3$ with their estimated standard deviations in parentheses.

(a) Bond Lengths (Å)

Ga-O11	1.962(7)	C21-C23	1.474(13)
Ga-O12	1.913(7)	C23-C26	1.448(17)
Ga-O21	1.968(7)	C26-C27	1.396(19)
Ga-O22	1.943(7)	C27-C28	1.347(23)
Ga-O31	1.971(7)	C28-S21	1.744(14)
Ga-O32	1.968(7)	S21-C23	1.710(14)
O11-C11	1.233(13)	C23-C24	1.534(17)
O11-C12	1.440(16)	C24-F21	1.300(16)
C12-C13	1.423(17)	C24-F22	1.317(16)
C13-O12	1.238(14)	C24-F23	1.284(13)
C11-C13	1.457(15)	O31-C31	1.270(13)
C15-C16	1.366(15)	C31-C32	1.459(16)
C16-C17	1.430(17)	C32-C33	1.362(17)
C17-C18	1.383(19)	C33-O32	1.281(14)
C18-S11	1.640(14)	C31-C35	1.436(16)
S11-C13	1.736(11)	C35-C36	1.384(16)
C13-C14	1.522(18)	C36-C37	1.408(18)
C14-F11	1.333(17)	C37-C38	1.334(19)
C14-F12	1.226(17)	C38-S31	1.678(13)
C14-F13	1.238(16)	S31-C35	1.738(12)
O21-C21	1.259(13)	C33-C34	1.496(18)
C21-C22	1.410(16)	C34-F31	1.275(14)
C22-C23	1.358(13)	C34-F32	1.233(16)
C23-O22	1.292(13)	C34-F33	1.339(18)

(b) Non-bonded Contacts (Å)

O11-O12	2.791(10)	O12-O31	2.658(10)
O11-O21	2.744(10)	O21-O22	2.786(10)
O11-O31	2.732(10)	O21-O32	2.827(9)
O11-O32	2.670(10)	O22-O31	2.820(10)
O12-O21	2.756(10)	O22-O32	2.707(10)
O12-O22	2.839(10)	O31-O32	2.817(10)

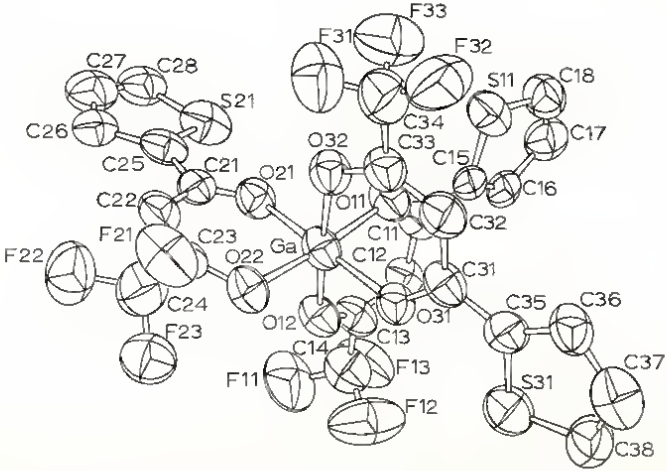
(c) Bond Angles (°)

O11-Ga-O12	92.1(3)	C11-C15-C16	133.6(10)
O11-Ga-O21	88.6(3)	S11-C15-C16	112.1(8)
O11-Ga-O22	173.1(3)	C15-C16-C17	109.8(10)
O11-Ga-O31	88.8(3)	C16-C17-C18	113.3(12)
O11-Ga-O32	85.6(3)	C17-C18-S11	113.0(10)

Table 17. Continued.

O11-Ga-O32	85.6(3)	C17-C18-S11	113.0(10)
O12-Ga-O21	90.4(3)	C18-S11-C15	91.7(6)
O12-Ga-O22	94.8(3)	C13-C14-F11	107.8(11)
O12-Ga-O31	86.3(3)	C13-C14-F12	115.1(12)
O12-Ga-O32	176.7(3)	C13-C14-F13	117.7(12)
O21-Ga-O22	90.5(3)	F11-C14-F12	102.6(12)
O21-Ga-O31	175.7(3)	F11-C14-F13	103.3(11)
O21-Ga-O32	91.8(3)	F12-C14-F13	108.6(12)
O22-Ga-O31	92.2(3)	Ga-O21-C21	127.1(7)
O22-Ga-O32	87.6(3)	O21-C21-C22	124.2(10)
O31-Ga-O32	91.3(3)	O21-C21-C25	115.6(10)
Ga-O11-C11	127.9(7)	C25-C21-C22	120.2(10)
O11-C11-C12	124.5(10)	C21-C22-C23	122.0(10)
O11-C11-C15	118.0(10)	C22-C23-O22	129.5(10)
C15-C11-C12	117.5(10)	C22-C23-C24	120.4(10)
C11-C12-C13	119.0(10)	C24-C23-O22	110.0(10)
C12-C13-O12	131.4(10)	C23-O22-Ga	121.8(6)
C12-C13-C14	112.5(10)	C21-C25-S21	119.1(9)
C14-C13-O12	116.1(10)	C21-C25-C26	127.2(10)
C13-O12-Ga	124.5(7)	S21-C25-C26	113.7(9)
C11-C15-S11	114.3(8)	C25-C26-C27	106.7(11)
C26-C27-C28	118.2(13)	C34-C33-O32	112.0(10)
C27-C28-S21	110.4(11)	C33-O32-Ga	121.3(7)
C28-S21-C25	90.8(6)	C31-C35-S31	118.1(8)
C23-C24-F21	110.1(10)	C31-C35-C36	129.0(10)
C23-C24-F22	112.0(10)	S31-C35-C36	111.9(8)
C23-C24-F23	113.2(10)	C35-C36-C37	109.1(10)
F21-C24-F22	107.3(11)	C36-C37-C38	115.8(12)
F21-C24-F23	106.9(11)	C37-C38-S31	111.3(10)
F22-C24-F23	106.9(10)	C38-S31-C35	91.8(6)
Ga-O31-C31	128.9(7)	C33-C34-F31	113.3(12)
O31-C31-C32	122.4(10)	C33-C34-F32	118.3(12)
O31-C31-C35	119.1(10)	C33-C34-F33	110.4(12)
C35-C31-C32	118.6(10)	F31-C34-F32	113.6(13)
C31-C32-C33	120.8(11)	F31-C34-F33	95.2(12)
C32-C33-O32	133.3(11)	F32-C34-F33	102.9(12)
C32-C33-C34	114.5(11)		

Figure 6 An ORTEP drawing of $Ga(ttfacac)_3$ showing the atomic numbering and thermal ellipsoids


F33
F31
F32
C27
C28
S11
C18
S21
C34
C26
C17
O32
C33
C15
C25
C21
O21
C16
C22
O11
C11
C32
F21
C23
Ga
F22
O22
C12
C31
C24
C35
C36
O12
O31
C13
F23
C14
C37
F13
F11
S31
F12
C38

Sterically, the trans isomer is greatly favoured because it affords smaller steric interactions with the thienyl rings

Three previous structure determinations have been reported on compounds containing ttfacac. In most cases, the metal "thienyl-oxygen" distance is either the same as the metal "perfluoro-oxygen" distance or 1σ to 2σ shorter (2.45(2), 2.42(2), 2.44(2), and 2.46(2) Å versus 2.45(2), 2.45(2), 2.49(2) and 2.48(2) Å for $(NH_4)Pr(ttfacac)_4 \cdot H_2O$;[76] 1.914(3) and 1.915(5) Å versus 1.929(5) and 1.920(5) Å for $Cu(ttfacac)_2$,[77] 2.096(4) versus 2.077(4) Å for $(\phi_3P)_2Cu(ttfacac)$)[77] Only in the case where large steric interactions occur ($(\phi_3P)_2Cu(ttfacac)$) between the thienyl ring and other ligands in the metal "thienyl-oxygen" distance longer.[77] The metal "thienyl-oxygen" distances in $Ga(ttfacac)_3$ are 1.962(7), 1.958(7) and 1.971(7) Å, while the metal "perfluoro-oxygen" distances are 1.915(7), 1.943(7) and 1.968(7) Å, respectively All metal "thienyl-oxygen" distances vary by less than 1.5σ and are not significantly different. Metal "perfluoro-oxygen" distances, however, all vary by 3σ or more and are, therefore, all significantly different Furthermore, in the first two ligands, the metal "thienyl-oxygen" distance is significantly longer than the metal "perfluoro-oxygen" distance This difference is contrary to most of the previous structural work,[76,77] and also the fact that the "thienyl-oxygen" is a better donor than the "perfluoro-oxygen." The trend of metal-oxygen distances in $Ga(ttfacac)_3$ also occurs in $(\phi_3P)_2Cu(ttfacac)$, a sterically hindered compound.[77]

The reason for the gallium-oxygen distances in $Ga(ttfacac)_3$ may well be the dominance of steric over electronic properties. Steric hindrance due to the thienyl rings likely accounts for the stability of

TABLE 18. Least-squares planes for $Ga(tfacac)_3$ in orthogonal coordinates. The title and equation of the plane are given, followed by the atoms with their deviations ($\times 10^{+3}$) from the plane (in Å) in parentheses. The atoms used to define the plane are noted by an asterisk following the deviation.

I Ligand Backbone (011, 012, C11, C12, C13)
-0.5298X +0.8479Y - 0.0194Z = 0.9534
Ce(122), 011(-16)*, 012(11)*, C11(23)*, C12(-10)*, C13(-7)*, C14(5), C15(107)

II Ligand Backbone (021, 022, C21, C22, C23)
0.7049X + 0.7084Y + 0.0372Z = 3.4746
Ce(198), 021(44)*, 022(-30)*, C21(-61)*, C22(24)*, C23(24)*, C24(196), C25(-250)

III Ligand Backbone (031, 032, C31, C32, C33)
0.2256X - 0.1376Y + 0.9645Z = 0.7707
Ce(272), 031(-7)*, 032(6)*, C31(9)*, C32(-2)*, C33(-6)*, C34(-156), C35(32)

IV Thiophene Ring (S11, C15, C16, C17, C18)
-0.5896X + 0.8069Y - 0.0511Z = 0.5782
S11(-11)*, C11(14), C15(7)*, C16(0)*, C17(-11)*, C18(14)*

V Thiophene Ring (S21, C25, C26, C27, C28)
0.7714X + 0.6357Y + 0.0292Z = 3.5747
S21(-6)*, C21(64), C25(16)*, C26(-21)*, C27(17)*, C28(-6)*

VI Thiophene Ring (S31, C35, C36, C37, C38)
0.2527X - 0.0660Y + 0.9653Z = 1.3000
S31(-5)*, C31(-68), C35(-4)*, C36(14)*, C37(-20)*, C38(15)*

VII Ring Through Ce, 011, 012
-0.5583X + 0.8269Y + 0.0665Z = 1.0188
Ce(0)*, 011(0)*, 012(0)*

VIII Ring Through Ce, 021, 022
0.7994X + 0.5674Y - 0.1978Z = 3.4970
Ce(0)*, 021(0)*, 022(0)*

IX Ring Through Ce, 031, 032
0.2504X + 0.0558Y + 0.9663Z = 1.6767
Ce(0)*, 031(0)*, 032(0)*

Dihedral angles between planes I-VI, II-V, III-VI, I-VII, II-VIII and III-IX are 4°29', 5°40', 4°23', 5°20', 16°40' and 11°25' respectively

the rings lesmec an null. The dihedral angles between planes Ga, OR1, OR2, and OR1, OR2, CR1, CR2, CR3, (R = 1,2,3) gives an some measure of the ligand distortion. In $Cu(ttfacac)_2$, a square planar complex, these angles are less than 1°. However $(\phi_3P)_2Cu(ttfacac)$[77] has a dihedral angle of 12°43', while $(NH_4)Fe(ttfacac)_4 \cdot H_2O$[76] has dihedral angles ranging from 10°-23°. In the latter case, these were attributed to crystal packing forces, but it is conceivable that they could be due to intramolecular steric repulsions. With $Ga(ttfacac)_3$, the dihedral angles are 5°20', 11°25' and 16°40'. The ligand with the smallest dihedral angle also has the shortest metal 'thienyl-oxygen' and metal "pacfluoro-oxygen" distances. This apparent cis effect may be due to ligand distortions caused by steric interactions.

The distances and angles in the these ligands are similar to those found in other structures. The thienyl ring is oriented with the sulphur atom cis to the oxygen atom as is found in $(NH_4)Fe(ttfacac)_4 \cdot H_2O$ and $Cu(ttfacac)_2$.[77] This orientation may be due to a sulphur-oxygen interaction, since the SN1-ON1 (N = 1-3) distances 2.812(8), 2.873(11) and 2.905(8) Å are shorter than the sum of the sulphur-oxygen van der Waals radii, 3.25 Å. The tilt of the thienyl rings with respect to the ON1, ON2, CN1, CN2, CN3 (N = 1-3), rings are 4°29', 5°40' and 4°23'. These angles are much larger than those found for $Cu(ttfacac)_2$[77] (~0°) and $(\phi_3P)_2Cu(ttfacac)$[77] (2°2'), and similar to those found in $(NH_4)Fe(ttfacac)_4 \cdot H_2O$[26] (2.6°, 2.3°, 6.3° and 12.4°). The degree of tilt of the thienyl ring is consistent with the larger steric interactions.

This compound revealed little about the electronic properties of gallium(III), except that they may be insignificant in this case. Steric factors seem to be the major factors to consider.

CHAPTER 6

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS(N,N-DIETHYLDITHIOCARBONATO)GALLIUM(III)

Complexes with sulphur ligands have received a great deal of attention lately since they can be studied as model compounds for complex biological systems.[78] Dithiolene complexes of tungsten, molybdenum, rhenium and vanadium are also of theoretical interest since they have trigonal prismatic geometries.[79] A common type of coordination compound with an MS_6 core is $M(dtc)_3$, (M = V, Cr, Mn, Fe, Co, Ga, In, Au),[79] these studied by x-ray diffraction are distorted octahedral species (Mn, Fe, Co, In, Au).[80,81,82,44,83]

Sulphur is quite large relative to oxygen and nitrogen and has a correspondingly large vanderWaals radius[84] which should give rise to large inter-ligand repulsions. With the small size of the gallium(III) ion,[5] this may be important in determining the final geometry in the coordination sphere. Since the structure of $In(dtc)_3$ has been reported,[44] a comparison of the indium derivative with the corresponding gallium compound will provide data on the effects of vanderWaals on coordination geometry. Therefore, the determination of the structure of $Ga(dtc)_3$ was undertaken.

Solution of Structure of $Ga(dtc)_3$

A sharpened three-dimensional Patterson function was calculated. The cell constants and space groups of $In(dtc)_3$ and $Ga(dtc)_3$ were

Table 19 Final positional and thermal parameters ($\times 10^{+4}$) for non-hydrogen atoms in $Ga(dmtc)_3$ with their estimated standard deviations in parentheses.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ga	2500^{+}	362(2)	0^{+}	45(2)	59(2)	37(1)	0^{+}	2(1)	0^{+}
S1	3092(2)	- 96(2)	1523(2)	39(1)	72(3)	31(1)	25(3)	6(2)	-10(3)
S2	3850(2)	-1121(2)	310(2)	48(2)	66(3)	31(1)	31(3)	18(2)	8(3)
S3	3499(2)	2267(2)	47(2)	41(2)	55(3)	48(1)	-11(3)	10(2)	- 6(3)
N1	4570(6)	-1800(8)	1933(5)	40(5)	77(9)	40(4)	31(11)	-18(8)	24(10)
N2	2500^{+}	4432(9)	0^{+}	63(9)	46(12)	50(6)	0^{+}	23(12)	0^{+}
C1	3916(7)	-1100(9)	1327(6)	36(6)	62(10)	41(5)	- 4(13)	7(9)	-14(13)
C2	5319(8)	-2589(11)	1763(8)	52(7)	86(12)	56(6)	50(16)	9(11)	- 3(14)
C3	6253(8)	-1767(14)	1397(10)	40(6)	180(18)	123(10)	7(17)	53(13)	-81(23)
C4	4596(6)	-1826(11)	2799(6)	70(8)	149(15)	22(5)	19(17)	- 4(9)	34(13)
C5	4102(10)	-3103(13)	2927(9)	112(11)	149(16)	70(8)	-38(22)	61(15)	57(18)
C6	2500^{+}	3193(12)	0^{+}	52(9)	49(15)	27(6)	0^{+}	- 6(12)	0^{+}
C7	1591(8)	5200(10)	- 84(9)	98(9)	69(10)	88(8)	92(17)	58(14)	43(15)

Table 19, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C8	1574(14)	5521(15)	772(10)	176(16)	75(21)	76(8)	76(30)	139(20)	-48(22)

† Value determined by the space group symmetry.

Table 20 Hydrogen atom positions in tris(diethyldithiocarbamate) gallium(III). The hydrogen atom is given followed by the atom to which it is bonded, the bond distance (in Å), the positional parameters (x 10^{+3}) and the isotropic thermal parameter (in $Å^2$).

Atom	Bonded to	Distance	x	y	z	B
H3	C3	1.96	673	-206	178	7.73
H3'	C3	1.03	680	-238	238	7.73
H3"	C3	0.89	646	-104	230	7.73
H5	C5	1.18	423	-418	276	7.53
H5'	C5	0.90	346	-295	266	7.53
H5"	C5	0.86	425	-317	346	7.53
H7	C7	0.94	151	597	-40	6.90
H7'	C7	0.67	202	489	4	6.90
H8	C8	1.08	223	605	116	8.54
H8'	C8	1.18	152	465	100	8.54
H8"	C8	0.89	117	606	89	8.54

Table 21 Observed and calculated structure factors for $Ga(dstc)_3$. The three columns in each group contain the values, reading from left to right, of l, $5F_{obs}$ and F_{calc}. A negative F_{obs} indicates an unobserved reflection which was not included in the least-squares refinement.

similar and the structures were thought to be isomorphous. The Ga-Ga, Ga-S and S-S vectors were rationalized based on the fractional coordinates of corresponding atomic positions in the structure of $In(dstr)_3$. These vectors were all present in the Patterson map. A Fourier synthesis phased on the Ga and three sulphur atoms was calculated and was used to locate all non-hydrogen atoms. The positions were similar to those in $In(dstr)_3$, R = 0.17. Three full-matrix least-squares cycles with individual isotropic thermal parameters were calculated, R = 0.13. Three full-matrix least-squares cycles with individual anisotropic thermal parameters refined the model to R = 0.077. A difference Fourier synthesis was computed and eleven of the fifteen hydrogen atoms were located. These hydrogen atoms were arbitrarily assigned isotropic thermal parameters one unit larger than the atom to which they are bonded. Three further full-matrix least-squares cycles with individual anisotropic thermal parameters for non-hydrogen atoms and hydrogen atoms held constant refined the model to R = 0.073. Since all shifts in positional and thermal parameters were one-fifth less than their respective estimated standard deviations, the model was considered refined.

Results and Discussion

Final positional and thermal parameters for non-hydrogen atoms are given in Table 19; those for hydrogen atoms are found in Table 20. Calculated and observed structure factors are listed in Table 21. Table 22 contains bond lengths, non-bonded contacts and bond angles for the molecule. Figure 7 is an ORTEP[71] diagram of the molecule and shows the atomic numbering scheme used. An idealized view of the coordination sphere of the molecule showing its approximate D_3 symmetry is given in Figure 8.

Table 22 Bond lengths, non-bonded contacts and bond angles for $Ga(detc)_3$ with their estimated standard deviations in parentheses

(a) Bond Lengths (Å)

Ga-S1	2.463(3)	C6-N2	1.278(16)
Ga-S2	2.408(3)	N1-C2	1.493(15)
Ga-S3	2.435(3)	N1-C4	1.471(13)
S1-C1	1.730(11)	N2-C7	1.522(15)
S2-C1	1.710(10)	C2-C3	1.539(18)
S3-C6	1.733(8)	C4-C5	1.557(19)
C1-N1	1.328(13)	C7-C8	1.516(22)

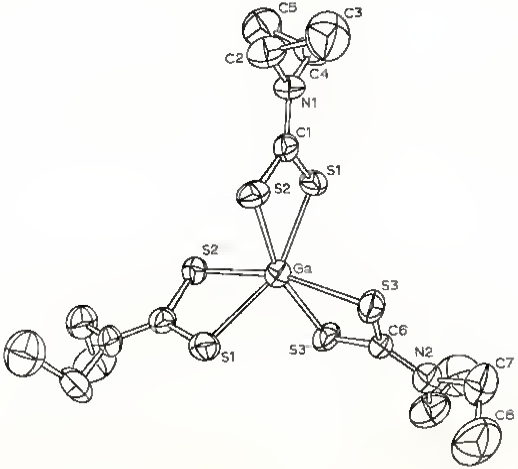
(b) Non-bonded Contacts (Å)

S1-S2	2.918(4)	S1-S3	3.720(5)
S3-S3'	2.910(4)	S1-S3'	3.717(5)
S1-S2'	3.513(5)	S2-S2'	3.734(5)
S2-S3	3.515(5)		

(c) Bond Angles (°)

S1-M-S2	73.61(9)	S1-C1-S2	116.1(6)
S3-M-S3'	73.41(10)	S3-C6-S3'	114.2(4)
S1-M-S3	98.88(10)	S1-C1-N1	121.8(8)
S1-M-S3'	98.74(10)	S2-C1-N1	122.1(8)
S1-M-S2'	92.34(9)	S3-C6-N2	122.9(6)
S2-M-S3	93.08(10)	C1-N1-C2	120.9(9)
S2-M-S2'	101.67(10)	C1-N1-C4	121.9(9)
S1-M-S1'	157.98(10)	C6-N2-C7	121.2(7)
S2-M-S3'	164.53(10)	N1-C2-C3	108.5(10)
M-S1-C1	84.0(4)	N1-C4-C5	109.2(10)
M-S2-C1	86.2(4)	N2-C7-C8	111.4(11)
M-S3-C6	88.2(3)	C2-N1-C4	117.2(8)

Figure 7. An ORTEP drawing of $Ge(detc)_3$ showing the atomic numbering and thermal e[illegible]


C5
C3
C2
C4
N1
C1
S1
S2
S2
Ga
S3
C6
S3
N2
C7
S1
C8

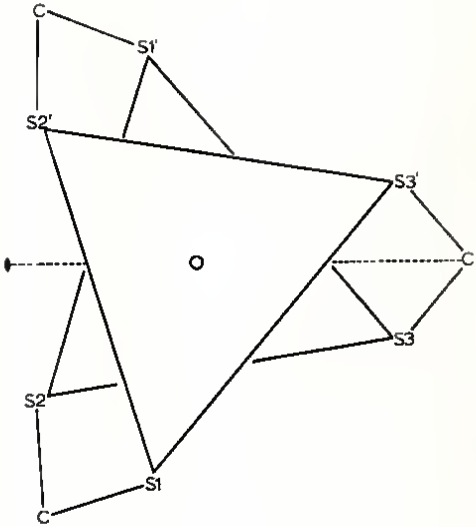
The structure consists of distinct $Co(detc)_3$ molecules separated by normal intermolecular Van der Waals contacts. With four $Co(detc)_3$ molecules per unit cell, the space group symmetry requires that the molecule sit on a two-fold axis.[58] $Co(detc)_3$ is very distorted from ideal octahedral geometry (Figures 7 and 8), as are $In(detc)_3$,[44] $Fe(detc)_3$[81] and $Mn(detc)_3$.[80]

The distances and angles in the ligands (Table 22) are in agreement with the range and accuracy of the values found in other detc complexes[44,80,81] and in sodium detc.[85] Distances and angles do not compare well in the two ligands in this compound. This may be attributable to a space group ambiguity, although the $In(detc)_3$ refinement diverged when the acentric Cc space group was assumed.[44] The S_2CN moieties are planar (Table 23), the C1 - N1 distance of 1.328(13) Å is slightly longer than that found* in acetone-semicarbazone, 1.278(3) Å and the carbon-sulphur distances are also slightly longer than that found in acetone thiosemicarbazone,* 1.725(8), 1.729(8) and 1.736(6) Å versus 1.690(5). This is consistent with the following canonical structures contributing to the ligand:

The C6-N2 distance is considerably shorter than C1-N1 and can be attributed to a space group ambiguity.[44]

* G. J. Palenik, unpublished results.

Figure 8. An idealized view of the $Ga(datc)_3$ coordination sphere showing the approximate D_3 symmetry. The two-fold axis shown is imposed by the space group symmetry


C
S1'
S2'
S3'
C
S3
S2
S1
C

The gallium sulphur distances are 2.463(3), 2.408(3) and 2.435(3) Å. These distances are very similar to those found in $Fe(dtbdtc)_3$[86] (the average Fe-S distance 2.42 Å), a high spin iron (iii) compound. The six-coordinate ionic radius of iron(iii) (0.64 Å) compares well with that of gallium(iii) (0.62 Å).[5] The indium-sulphur distances in $In(detc)_3$,[44] 2.601(2), 2.571(2) and 2.589(2) Å are 0.17Å longer than the corresponding gallium distances, exactly the difference in the six coordinate ionic radii. This also implies the two metals interact similarly with sulphur ligands.

The ligand bites for $Ga(detc)_3$ are 2.918(4) and 2.910(4) Å which are slightly shorter than those found for $In(detc)_3$,[44] (2.956(3) and 2.954(4) Å) but well within the range found in $Mn(detc)_3$,[80] (2.89(1) to 2.96(1)Å). Ligand bite for detc is fairly constant and, as a result, the SMS angle and sulphur-sulphur inter-ligand distances or non-bonded contacts are a function of the metal size.

This effect of metal size is readily seen in a comparison of $Ga(detc)_3$ and $In(detc)_3$. The SMS angles decrease with increasing metal size, 73.61(9), 73.41°(10) versus 69.72(7), 69.54°(7) for M = Ga, In. The non-bonded contacts, however, increase with increasing metal size 3.62 versus 3.74 Å for Ga and In. While both these distances compare well with the sum of the sulphur van der Waals radii, 3.70 Å[84] the $Ga(detc)_3$ compound will have greater van der Waals forces affecting its geometry than will the larger In analogue.

Comparison of twist angles* for $Ga(detc)_3$ and $In(detc)_3$ show that the angle, ϕ, decreases with increasing metal size (36°48', 42°25' versus 30°56', 38°36', for Ga and In). The angle ϕ ranges from 0° for trigonal

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* See Chapter 12, these angles are calculated by method 1.

Table 23. Least-squares planes for $Ga(detc)_3$ in orthogonal coordinates. The title and equation of the plane are given, followed by the atoms with their deviations ($\times 10^{-3}$) from the plane (in Å) in parentheses. The atoms used to define the plane are noted by an asterisk following the deviation

I Plane Through S1, S2, C1, N1

$$0.6183X + 0.7584Y + 0.2061Z = 2.6397$$

Ga(-61), S1(1)*, S2(1)*, N1(2)*, C1(-4)*, C2(90), C3(1569), C4(66), C5(-1522)

II Plane Through S3, C6, N2

$$-0.0509X + 0.9987Z = 0.1890$$

Ga(0)†, S3(0)*, N2(0)*, C6(0)*, C7(-67), C8(1318)

† Ga, C6 and N2 all lie on a two fold axis, they are therefore colinear and coplanar.

prismatic geometry to 60° for octahedral geometry. Since the distortion from octahedral geometry increases with metal size, the nature of the distortion may be due to the decrease in non-bonded contacts. Deviations from octahedral symmetry depend on the ligand geometry and the size of the neutral metal atom.

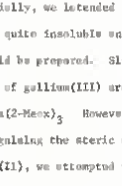
CHAPTER 7

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS(PICOLINATO)GALLIUM(III)MONOHYDRATE AND TRIS (6-METHYLPICOLINATO)GALLIUM(III)

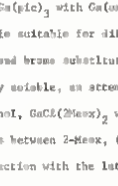
The structures of $GaCl_3terpy$[41] and $(GaCl_2bipy_2)GaCl_4$[40] have shown that the gallium-nitrogen bond lengths remain virtually constant, while the gallium-chlorine bond lengths vary slightly more. This variation may be due to greater size and polarizability of the chlorine atom. If a smaller, less polarizable ligand replaces chlorine in the coordination sphere of gallium, will gallium-nitrogen distances vary? To answer this question, we undertook the determination of the structure of $Ga(pic)_3 \cdot H_2O$.

Initially, we intended to compare $Ga(pic)_3$ with $Ga(ox)_3$, but the latter is quite insoluble and no crystals suitable for diffraction experiments could be prepared. Since methyl and bromo substituted quinolinate compounds of gallium(III) are reasonably soluble, an attempt was made to prepare $Ga(2\text{-Meox})_3$. However, in methanol, $GaCl(2Meox)_2$ was prepared.

Recognizing the steric similarities between 2-Meox, (I), and 6-Maplc, (II), we attempted the same reaction with the latter ligand. This led not to the expected $GaCl(6\text{-MepIc})_2$, but to $Ga(6\text{-MepIc})_3$.



(I)



(II)

Table 24. Final positional and thermal parameters ($\times 10^4$) for non-hydrogen atoms in $Ga(pic)_3 \cdot H_2O$ with their estimated standard deviations in parentheses. The parameters of the Ga atom are $\times 10^{+5}$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ga	11313(2)	21953(9)	12563(5)	27(1)	873(10)	222(3)	2(6)	-16(2)	6(13)
O1	1160(1)	2261(6)	2669(3)	4(1)	118(8)	23(2)	16(3)	6(2)	4(7)
O2	1526(1)	3948(5)	1291(3)	4(1)	95(8)	23(2)	8(3)	- 4(2)	-20(7)
O3	736(1)	383(5)	1099(3)	3(1)	76(7)	35(3)	6(3)	- 2(2)	7(7)
N1	1678(2)	743(6)	1566(3)	2(1)	93(9)	17(3)	- 7(4)	- 2(2)	-24(8)
N2	1194(1)	2408(6)	-201(3)	2(1)	77(9)	23(3)	- 1(3)	- 3(2)	- 9(8)
N3	537(2)	3336(6)	1204(3)	2(1)	53(8)	21(3)	- 3(3)	0(2)	1(7)
O1'	1589(2)	1703(7)	3989(3)	10(1)	197(11)	15(2)	31(4)	- 1(2)	- 8(8)
O2'	1999(2)	5276(6)	426(4)	6(1)	158(10)	44(3)	-40(4)	- 5(2)	16(9)
O3'	34(1)	-401(6)	1183(4)	4(1)	100(9)	75(4)	-20(3)	3(2)	33(9)
C1	1917(2)	- 68(9)	973(5)	2(1)	115(12)	28(4)	4(5)	1(3)	-32(11)
C2	2304(2)	-889(10)	1317(8)	6(1)	136(14)	48(5)	24(6)	10(3)	-29(13)
C3	2436(2)	-839(9)	2281(6)	3(1)	131(14)	55(5)	18(5)	- 3(3)	12(13)
C4	2181(2)	- 17(9)	2889(5)	7(1)	105(13)	30(4)	13(5)	- 6(3)	15(12)

Table 24, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C5	1810(2)	739(7)	2509(4)	3(1)	71(10)	15(3)	- 1(4)	-5(2)	13(9)
C6	1504(2)	1631(8)	3135(4)	4(1)	87(11)	14(3)	1(4)	2(2)	22(9)
C7	972(2)	1654(8)	- 933(5)	4(1)	81(11)	28(4)	1(4)	-5(3)	- 6(10)
C8	1037(2)	1599(9)	-1885(5)	6(1)	103(12)	22(3)	13(5)	-9(3)	- 5(11)
C9	1334(2)	3160(9)	-2065(5)	7(1)	135(14)	19(4)	18(5)	5(3)	1(11)
C10	1564(2)	3934(9)	-1300(5)	5(1)	118(13)	25(4)	- 6(5)	2(3)	22(11)
C11	1476(2)	3552(8)	- 383(4)	1(1)	83(10)	25(4)	0(4)	-4(2)	13(10)
C12	1700(2)	4360(8)	506(5)	3(1)	82(11)	29(4)	-10(5)	-9(3)	17(10)
C13	459(2)	4861(8)	1223(4)	4(1)	81(11)	24(4)	- 2(5)	5(3)	17(10)
C14	24(2)	5471(8)	1254(5)	5(1)	84(12)	33(4)	15(5)	-1(3)	- 8(11)
C15	-325(2)	4419(9)	1276(5)	5(1)	128(14)	32(4)	22(5)	-1(3)	6(12)
C16	-244(2)	2854(9)	1250(5)	6(1)	109(11)	26(4)	- 4(6)	2(3)	14(12)
C17	189(2)	2321(8)	1204(4)	2(1)	104(11)	22(3)	13(4)	-1(2)	7(10)
C18	303(2)	645(8)	1164(4)	5(1)	98(12)	22(4)	- 5(5)	-2(3)	17(10)
OW	3914(2)	2422(7)	4484(4)	11(1)	127(10)	67(4)	9(4)	22(3)	-33(10)

Table 23. Final parameters for the hydrogen atoms in $Co(pic)_3 \cdot H_2O$. The hydrogen atom is given followed by the atom to which it is bonded. The corresponding bond distances (in Å), the positional parameters ($\times 10^3$) and the isotropic thermal parameters (in $Å^2$) follow.

Atom	Bonded to	Distance	x	y	z	B
H1	C1	1.02	181	0	26	2.81
H2	C2	1.03	248	-147	82	4.37
H3	C3	1.12	271	-146	273	4.14
H4	C4	0.93	226	1	355	3.68
H7	C7	0.97	78	84	-72	2.98
H8	C8	1.08	86	145	-250	3.41
H9	C9	0.98	143	339	-270	3.43
H10	C10	1.09	177	495	-142	3.46
H13	C13	0.94	69	556	111	3.03
H14	C14	0.96	0	639	122	3.54
H15	C15	1.12	-47	477	141	3.66
H16	C16	1.07	-46	188	136	3.42
HW1	OW	1.01	372	263	502	5.45
HW2	OW	1.17	407	367	441	5.45

Table 26 Observed and calculated structure factors for $Ga(pic)_3 \cdot H_2O$. The three columns in each group contain the values, reading from left to right, of h, $5F_{obs}$ and $5F_{obs}$ and $5F_{calc}$. A negative F_{obs} indicates an unobserved reflection which was not included in the least-squares refinement.

Table 27. Bond lengths, non-bonded contacts and bond angles for $Ga(pic)_3 \cdot H_2O$ with their estimated standard deviations in parentheses.

(a) Bond Lengths (Å)

Ga-O1	1.955(4)	C8-C9	1.375(10)
Ga-O2	1.936(4)	C9-C10	1.387(10)
Ga-O3	1.955(4)	C10-C11	1.371(9)
Ga-N1	2.073(5)	C11-N2	1.333(8)
Ga-N2	2.083(5)	C11-C12	1.524(9)
Ga-N3	2.033(5)	C12-O2	1.298(8)
N1-C1	1.339(8)	C12-O2'	1.206(8)
C1-C2	1.406(10)	N3-C13	1.325(9)
C2-C3	1.369(11)	C13-C14	1.413(9)
C3-C4	1.387(10)	C14-C15	1.385(10)
C4-C5	1.357(9)	C15-C16	1.361(11)
C5-N1	1.342(8)	C16-C17	1.387(9)
C5-C6	1.529(9)	C17-N3	1.360(8)
C6-O1	1.289(7)	C17-C18	1.480(10)
C6-O1'	1.203(7)	C18-O3	1.315(7)
N2-C7	1.337(8)	C18-O3'	1.210(8)
C7-C8	1.393(9)		

(b) Non-bonded Contacts (Å)

O1-O2	2.735(6)	O2-N3	3.018(6)
O1-O3	2.917(6)	O3-N1	2.868(6)
O1-N1	2.633(6)	O3-N2	2.941(6)
O1-N3	2.802(6)	O3-N3	2.601(7)
O2-N1	2.832(7)	N1-N2	3.095(7)
O2-N2	2.605(6)	N2-N3	3.016(7)

(c) Bond Angles (°)

O1-Ga-O2	89.3(2)	Ga-N2-C7	128.9(4)
O1-Ga-O3	96.5(2)	Ga-N2-C11	111.6(4)
O1-Ga-N1	81.6(2)	C11-N2-C7	119.3(5)
O1-Ga-N2	169.8(2)	N2-C7-C8	121.6(6)
O1-Ga-N3	89.3(2)	C7-C8-C9	118.6(6)
O2-Ga-O3	174.2(2)	C8-C9-C10	119.4(6)
O2-Ga-N1	89.8(2)	C9-C10-C11	118.7(6)
O2-Ga-N2	80.7(2)	C10-C11-N2	122.3(6)
O2-Ga-N3	99.0(2)	N2-C11-C12	114.8(5)
O3-Ga-N1	90.8(2)	C10-C11-C12	122.9(6)
O3-Ga-N2	93.5(2)	C11-C12-O2	113.3(5)
O3-Ga-N3	81.4(2)	C11-C12-O2'	119.9(6)
N1-Ga-N2	96.3(2)	O2'-C12-O2	126.8(6)
N1-Ga-N3	167.2(2)	C12-O2-Ga	118.2(4)

Table 27, continued

O1'-C6-O1	126.0(6)	Ga-N3-C13	128.9(4)
C6-O1-Ga	117.0(4)	Ga-N3-C17	111.6(4)
N2-Ga-N3	94.3(2)	C17-N3-C13	119.3(5)
Ga-N1-C1	130.3(4)	N3-C13-C14	122.0(6)
Ga-N1-C5	110.9(4)	C13-C14-C15	117.8(6)
C5-N1-C1	118.8(5)	C14-C15-C16	120.0(7)
N1-C1-C2	121.4(6)	C15-C16-C17	119.7(6)
C1-C2-C3	118.6(7)	C16-C17-N3	121.1(6)
C2-C3-C4	119.4(7)	N3-C17-C18	115.3(5)
C3-C4-C5	119.0(8)	C16-C17-C18	123.6(6)
C4-C5-N1	122.9(6)	C17-C18-O3	114.2(5)
N1-C5-C6	114.9(5)	C17-C18-O3'	122.8(6)
C4-C5-C6	122.1(6)	O3'-C18-O3	123.0(6)
C5-C6-O1	114.7(5)	C18-O3-Ga	116.4(4)
C5-C6-O1'	119.3(6)		

Table 28. Least-squares planes for $Ca(pic)_3 \cdot H_2O$ in orthogonal coordinates. The title and equation of the plane are given, followed by the atoms with their deviations ($\times 10^{+3}$) from the plane (in Å) in parentheses. The atoms used to define the plane are noted by an asterisk following the deviation.

I Pyridine Ring (N1, C1, C2, C3, C4, C5)
0.5626X + 0.8166Y - 0.1293Z = 2.9559
Ca(173), O1(-86), N1(10)*, O1'(-63), C1(-2)*, C2(-7)*, C3(9)*, C4(-2)*, C5(-8)*, C6(-61)

II Pyridine Ring (N2, C7, C8, C9, C10, C11)
0.7359X - 0.6766Y + 0.0252Z = 1.2516
Ca(-91), O2(-256), N2(11)*, O2'(98), C7(-2)*, C8(-2)*, C9(-4)*, C10(13)*, C11(-17)*, C12(-38)

III Pyridine Ring (N3, C13, C14, C15, C16, C17)
0.0323X - 0.0189Y + 0.9993Z = 1.6604
Ca(170), O3(-71), N3(7)*, O3'(-10), C13(2)*, C14(-8)*, C15(6)*, C16(3)*, C17(-10)*, C18(-27)

IV Carboxylate Group (O1, O1', C6)
0.5422X + 0.8309Y - 0.1252Z = 2.8489
O1(0)*, O1'(0)*, C6(0)*

V Carboxylate Group (O2, O2', C12)
-0.6546X + 0.7391Y - 0.1589Z = -0.6629
O2(0)*, O2'(0)*, C12(0)*

VI Carboxylate Group (O3, O3', C18)
0.0646X - 0.0307Y + 0.9974Z = 1.6494
O3(0)*, O3'(0)*, C18(0)*

VII Ligand Backbone (O1, N1, C5, C6)
0.5376X + 0.8358Y - 0.1120Z = 2.0934
Ca(221), O1(-1)*, N1(1)*, O1'(16), C5(-1)*, C6(1)*

VIII Ligand Backbone (O2, N2, C11, C12)
0.7170X - 0.6834Y + 0.1374Z = 1.1197
Ca(165), O2(-30)*, N2(25)*, O2'(153), C11(-30)*, C12(51)*

IX Ligand Backbone (O3, N3, C17, C18)
0.0499X - 0.0407Y + 0.9979Z = 1.6227
Ca(221), O3(-6)*, N3(6)*, O3'(32), C17(-10)*, C18(11)*

X Plane Through Ga, O1, N1

$$0.6104X + 0.7921Y + 0.0062Z = 3.4765$$

Ga(O)*, O1(O)*, N1(O)*

XI Plane Through Ga, O2, N2

$$0.7874X - 0.6098Y + 0.0904Z = 1.5682$$

Ga(O)*, O2(O)*, N2(O)*

XII Plane Through Ga, O3, N3

$$-0.0919X - 0.0795Y + 0.9926Z = 1.3016$$

Ga(O)*, O3(O)*, N3(O)*

Dihedral angles between planes I-IV, II-V, III-VI, VII-X, VIII-XI and IX-XII are 1°27', 9°40', 1°58', 8°20', 6°26' and 8°26' respectively.

$Ga(6\text{-Mepic})_3$ and $Ga(pic)_3$ make an interesting comparison, since 6-Mepic has a bulky methyl group, which will cause steric repulsions in the coordination sphere. To study the effect of the methyl group on the coordination sphere, we also undertook the determination of the structure of $Ga(6\text{-Mepic})_3$

Solution of Structure of $Ga(pic)_3 \cdot H_2O$

A sharpened, three-dimensional, Patterson function was calculated from which the position of the Ga atom was determined. Successive Fourier syntheses allowed us to locate all non-hydrogen atoms, R = 0.45. Three full-matrix least-squares cycles with individual isotropic thermal parameters refined the model to R = 0.097. Three block-diagonal least-squares cycles with individual anisotropic thermal parameters were computed and the model refined to R = 0.066. A difference Fourier was calculated and all hydrogen positions were found. The hydrogen atoms were then arbitrarily assigned isotropic thermal parameters one unit larger than the atom to which they are bonded. The hydrogen atoms were then held constant as three block-diagonal least-squares cycles with individual anisotropic thermal parameters for non-hydrogen atoms were computed, R = 0.052. At that point, all shifts were one-tenth of their respective estimated standard deviations so that refinement of the model was considered complete.

Results for $Ga(pic)_3 \cdot H_2O$

Final positional and thermal parameters for non-hydrogen atoms are given in Table 24; those for hydrogen atoms are found in Table 25. Calculated and observed structure factors are listed in Table 26.

Table 27 contains bond-lengths, non-bonded contacts and bond angles for the molecule. Figure 9 is an ORTEP[71] diagram of the molecule which shows the atomic numbering scheme used.

Solution of Structure of $Ge(6\text{-}Maple)_3$

A sharpened, three-dimensional, Patterson function was calculated. In the Harker sections, the Harker plane vector and the Ga(2x, 2y, 2z) vector overlapped. The x and z coordinates for the Ga atom were estimated from the centroid of this poorly resolved peak and the y coordinate was fixed at a quarter. A Fourier synthesis was phased on the Ga atom only and, from this, two atoms in the coordination sphere were assigned. Care had to be taken to see that these atoms corresponded to a consistent set, since a pseudo-mirror existed at y = 1/4. Successive Fourier syntheses allowed us to locate all non-hydrogen atom positions, R = 0.17. Three full-matrix least-squares cycles with individual isotropic thermal parameters refined the model to R = 0.099. Three block-diagonal least-squares cycles with individual anisotropic thermal parameters refined the model further, R = 0.065. A difference Fourier synthesis was calculated and all hydrogen atom positions were determined. The hydrogen atoms were then arbitrarily assigned isotropic thermal parameters one unit larger than the atom to which they are bonded. The hydrogen atoms were then held constant and three block-diagonal least-squares cycles with individual anisotropic thermal parameters for non-hydrogen atoms were calculated, R = 0.045. At this stage, all shifts were one-tenth or less of their respective estimated standard deviations, so that the model was considered refined.

Table 29. Final positional and thermal parameters ($\times 10^{+4}$) for non-hydrogen atoms in $Ga(6\text{-Mapic})_3$ with their estimated standard deviations in parentheses. The parameters of the Ga atom are $\times 10^{+5}$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ga	38152(2)	25640(10)	13517(4)	59(1)	964(8)	401(3)	-39(7)	52(2)	44(16)
O1	3881(1)	2110(5)	2585(3)	10(1)	149(10)	47(2)	9(3)	0(2)	3(7)
O2	3367(1)	964(5)	1296(3)	10(1)	138(8)	46(2)	-21(3)	10(2)	- 8(7)
O3	4184(1)	4388(5)	1363(3)	5(1)	97(7)	83(3)	- 4(3)	7(2)	3(7)
N1	3336(1)	4159(6)	1793(3)	6(1)	116(9)	34(2)	- 5(3)	5(2)	- 2(8)
N2	3691(1)	2414(7)	- 54(3)	8(1)	120(8)	48(2)	18(5)	11(2)	8(11)
N3	4400(1)	1332(6)	1224(3)	7(1)	99(9)	51(3)	- 1(3)	2(2)	7(8)
O1'	3585(2)	2498(8)	3858(3)	25(1)	212(9)	40(2)	24(7)	8(2)	32(12)
O2'	2848(1)	-208(6)	501(4)	11(1)	233(11)	87(4)	-42(4)	5(2)	-60(10)
O3'	4868(1)	5156(6)	1449(5)	9(1)	144(9)	176(6)	-23(4)	13(3)	-20(12)
C1	3272(2)	3819(7)	2637(4)	9(1)	102(10)	38(3)	-12(4)	3(2)	-11(9)
C2	2942(2)	4505(8)	3083(4)	10(1)	150(12)	44(3)	- 8(5)	12(3)	-42(11)
C3	2677(2)	5598(9)	2651(5)	9(1)	211(15)	60(4)	- 3(5)	14(3)	-51(13)
C4	2758(2)	6013(8)	1820(4)	8(1)	171(13)	50(4)	17(5)	3(3)	- 4(12)

Table 29, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C5	3088(2)	5269(8)	1383(4)	7(1)	140(12)	42(3)	3(5)	1(2)	- 7(10)
C6	3173(2)	5693(8)	463(4)	10(1)	168(13)	52(4)	29(5)	9(3)	16(12)
C7	3596(2)	2725(8)	3070(4)	13(1)	121(12)	41(3)	-22(5)	- 4(2)	-11(11)
C8	3364(2)	1369(7)	- 207(4)	8(1)	123(11)	52(4)	15(5)	- 4(3)	-24(11)
C9	3229(2)	919(9)	-1028(5)	13(1)	189(15)	66(5)	28(6)	-11(3)	-38(14)
C10	3433(3)	1542(10)	-1738(5)	20(1)	20(16)	59(5)	38(7)	- 7(4)	-26(14)
C11	3752(2)	2585(11)	-1593(4)	19(1)	210(14)	48(3)	61(9)	17(3)	24(17)
C12	3891(2)	3047(7)	- 745(4)	11(1)	141(13)	56(4)	32(5)	21(3)	34(10)
C13	4243(2)	4214(10)	- 610(6)	14(1)	230(17)	87(5)	- 8(7)	38(4)	94(16)
C14	3169(2)	634(8)	569(4)	7(1)	140(12)	60(4)	- 1(5)	8(3)	-19(11)
C15	4725(2)	2390(9)	1333(4)	7(1)	123(10)	70(4)	8(6)	7(2)	0(15)
C16	5151(2)	1930(8)	1391(5)	8(1)	151(13)	84(5)	11(5)	6(3)	- 9(12)
C17	5247(2)	308(9)	1339(5)	8(1)	196(15)	93(6)	23(6)	3(3)	18(15)
C18	4917(2)	-779(8)	1213(5)	11(1)	142(13)	69(5)	23(5)	10(3)	-13(12)
C19	4489(2)	-254(8)	1154(4)	10(1)	143(12)	45(3)	5(5)	4(3)	0(11)

Table 29, continued . . .

Atom									
C20	4138(2)	-1429(8)	1005(5)	14(1)	111(12)	81(5)	4(5)	4(3)	-5(13)
C21	4596(2)	4112(8)	1402(5)	8(1)	136(13)	86(5)	-6(5)	5(3)	-1(13)

Table 30. Final parameters for the hydrogen atoms in $Ga(6\text{-Mepic})_3$. The hydrogen atom is given followed by the atom to which it is bonded. The corresponding bond distance (in Å), the positional parameters ($\times 10^3$) and the isotropic thermal parameters (in $Å^2$) follow

Atom	Bonded to	Distance	x	y	z	B
H2	C2	1.29	243	436	388	5.2
H3	C3	0.93	247	591	304	5.5
H4	C4	1.05	262	690	141	5.3
H6	C6	1.19	294	494	- 2	5.5
H6'	C6	1.03	295	658	59	5.5
H6"	C6	1.04	348	533	29	5.5
H9	C9	0.94	294	60	-116	6.6
H10	C10	1.12	322	115	-230	6.9
H11	C11	1.14	399	333	-197	6.7
H13	C13	0.80	414	487	- 30	6.6
H13'	C13	1.14	457	378	- 33	6.6
H13"	C13	1.19	439	483	-123	6.6
H16	C16	1.27	543	305	138	5.6
H17	C17	1.09	557	4	159	6.2
H18	C18	1.18	501	-214	131	5.8
H20	C20	1.05	399	-118	36	5.7
H20'	C20	0.90	395	-117	142	5.7
H20"	C20	0.97	420	-256	109	5.7

Table 31. Observed and calculated structure factors for $Ca(6\text{-Mepic})_3$. The three columns in each group contain the values, reading from left to right, of l, $5F_{obs}$, and $5F_{calc}$. A negative F_{obs} indicates an unobserved reflection which was not included in the least-squares refinement.

[illegible]

Table 32. Bond lengths, non-bonded contacts and bond angles for $Ga(6\text{-Hepic})_3$ with their estimated standard deviations in parentheses.

(a) Bond Lengths (Å)

Ga-O1	1.939(4)	C9-C10	1.385(11)
Ga-O2	1.927(4)	C10-C11	1.331(11)
Ga-O3	1.902(4)	C11-C12	1.413(9)
Ga-N1	2.126(4)	C12-N2	1.359(8)
Ga-N2	2.188(4)	C12-C13	1.472(10)
Ga-N3	2.102(4)	C8-C14	1.491(9)
N1-C1	1.351(7)	C14-O2	1.287(8)
C1-C2	1.388(8)	C14-O2'	1.221(8)
C2-C3	1.387(9)	N3-C15	1.347(8)
C3-C4	1.358(10)	C15-C16	1.378(8)
C4-C5	1.393(8)	C16-C17	1.385(10)
C5-N1	1.345(8)	C17-C18	1.377(10)
C5-C6	1.492(9)	C18-C19	1.399(9)
C1-C7	1.497(8)	C19-N3	1.354(8)
C7-O1	1.286(7)	C19-C20	1.479(9)
C7-O1'	1.230(7)	C15-C21	1.492(10)
N2-C8	1.352(8)	C21-O3	1.301(7)
C8-C9	1.369(10)	C21-O3'	1.212(8)

(b) Non-Bonded Contacts (Å)

O1-O2	2.677(6)	O2-N3	3.232(6)
O1-O3	2.856(6)	O3-N1	2.751(5)
O1-N1	2.667(6)	O3-N2	3.092(6)
O1-N3	2.787(6)	O3-N3	2.640(6)
O2-N1	2.769(6)	N1-N2	3.412(6)
O2-N2	2.634(6)	N2-N3	3.037(6)

(c) Bond Angles (°)

O1-Ga-O2	87.6(2)	C12-N2-C8	118.4(5)
O1-Ga-O3	96.0(2)	N2-C8-C9	122.6(6)
O1-Ga-N1	81.9(2)	C8-C9-C10	119.6(7)
O1-Ga-N2	164.9(2)	C9-C10-C11	118.2(7)
O1-Ga-N3	86.3(2)	C10-C11-C12	122.1(7)
O2-Ga-O3	170.6(2)	C11-C12-N2	119.1(6)
O2-Ga-N1	86.0(2)	N2-C12-C13	120.4(6)
O2-Ga-N2	79.4(2)	C11-C12-C13	120.6(6)
O2-Ga-N3	106.6(2)	N2-C8-C14	116.6(5)
N1-Ga-N2	104.6(2)	C9-C8-C14	120.6(6)
N1-Ga-N3	162.4(2)	C8-C14-O2	114.5(5)
N2-Ga-N3	90.1(2)	C8-C14-O2'	121.4(6)

Ga-N1-C1	107.9(3)	O2'-C14-O2	124.1(6)
Ga-N1-C5	132.4(4)	C14-O2-Ga	120.5(4)
C5-N1-C1	119.5(5)	Ga-N3-C15	108.6(4)
N1-C1-C2	122.6(5)	Ga-N3-C19	131.6(4)
C1-C2-C3	117.2(6)	C19-N3-C15	119.3(5)
C2-C3-C4	120.1(6)	N3-C15-C16	122.9(6)
C3-C4-C5	120.5(6)	C15-C16-C17	118.4(6)
C4-C5-N1	119.8(5)	C16-C17-C18	119.1(7)
N1-C5-C6	119.3(5)	C17-C18-C19	120.4(6)
C4-C5-C6	120.9(5)	C18-C19-N3	119.8(6)
N1-C1-C7	115.8(5)	N3-C19-C20	120.2(6)
C2-C1-C7	121.6(5)	C18-C19-C20	120.0(6)
C1-C7-O1	116.8(5)	N3-C15-C21	115.7(5)
C1-C7-O1'	119.3(6)	C16-C15-C21	121.5(6)
O1'-C7-O1	123.8(6)	C15-C21-O3	115.7(6)
C7-O1-Ga	116.2(4)	C15-C21-O3'	120.2(6)
Ga-N2-C8	108.3(4)	O3'-C21-O3	124.0(6)
Ga-N2-C12	133.1(4)	C21-O3-Ga	116.9(4)

Table 33. Least-squares planes for $Ga(6\text{-Mepic})_3$ in orthogonal coordinates. The title and equation of the plane are given, followed by the atoms with their deviations ($\times 10^{+3}$) from the plane (in Å) in parentheses. The atoms used to define the plane are noted by an asterisk following the deviation

I Pyridine Ring (N1, C1, C2, C3, C4, C5)
0.6105X + 0.7307Y + 0.3057Z = 9.6638
Ga(-273), N1(-22)*, C1(17)*, C2(6)*, C3(-24)*, C4(20)*, C5(3)*, C6(22), C7(157)

II Pyridine Ring (N2, C8, C9, C10, C11, C12)
-0.6510X + 0.7583Y - 0.0345Z = -5.9446
Ga(-184), N2(-4)*, C8(1)*, C9(3)*, C10(-6)*, C11(4)*, C12(1)*, C13(22), C14(-81)

III Pyridine Ring (N3, C15, C16, C17, C18, C19)
-0.0958X - 0.0912Y + 0.9912Z = 0.4545
Ga(284, N3(8)*, C15(-2)*, C16(-6)*, C17(9)*, C18(-3)*, C19(-5)*, C20(-41), C21(11)

IV Carboxylate Group (O1, O1', C7)
0.5788X + 0.7984Y + 0.1625Z = 8.9599
O1(0)*, O1'(0)*, C7(0)*

V Carboxylate Group (O3, O3', C21)
-0.5801X + 0.8084Y + 0.0956Z = -5.1854
O2(0)*, O2'(0)*, C14(0)*

VI Carboxylate Group (O3, O3', C21)
-0.0529X - 0.0309Y + 0.9981Z = 1.2957
O3(0)*, O3'(0)*, C21(0)*

VII Ligand Backbone (O1, N1, C1, C7)
0.5905X + 0.7672Y + 0.2503Z = 9.3970
Ga(-279), O1(-15)*, N1(14)*, C1(-25)*, C7(26)*

VIII Ligand Backbone (O2, N2, C8, C14)
-0.6362X + 0.7654Y + 0.0963Z = -5.7927
Ga(125), O2(-17)*, N2(17)*, C8(-30)*, C14(30)*

IX Ligand Backbone (O3, N3, C15, C21)
-0.0709X - 0.0999Y + 0.9925Z = 0.7969
Ga(219), O3(3)*, N3(-3)*, C15(5)*, C21(-5)*

X Plane Through Ga, O1, N1
0.6796X + 0.7272Y + 0.0968Z = 9.7635
Ga(0)*, O1(0)*, N1(0)*

Table 33, continued

XI Plane Through Ga, O2, N2

0.6922X - 0.7195Y - 0.0568Z = 6.[illegible]

Ga(0)*, O2(0)*, N2(0)*

XII Plane Through Ga, O3, N3

0.0706X - 0.0645Y + 0.9954Z = 2.7643

Ga(0)*, O3(0)*, N3(0)*

Dihedral angles between planes I-IV, II-V, II-VI, VII-X, VIII-XI and IX-XII are 9°15', 9°10', 4°15', 10°26', 4°43' and 8°22' respectively.

Results for $Ga(6\text{-}Mepir)_3$

Final positional and thermal parameters for non-hydrogen atoms are given in Table 29, those for hydrogen atoms are found in Table 30. Calculated and observed structure factors are found in Table 31. Table 32 lists bond lengths, non-bonded contacts and bond angles for the molecule. Figure 10 is an ORTEP[71] diagram of the molecule which shows the atomic numbering scheme used.

Discussion

Both $Ga(pir)_3$ and $Ga(6\text{-}Mepic)_3$ are molecular trans octahedral species (Figures 9 and 10). The distances in the ligands in both molecules compare well with each other and with the distances found in $Ni(pir)_2(H_2O)_2$[87] and $Cu(pir)_2$ hydrate.[88] The gallium-nitrogen distances in $Ga(pic)_3$ are 2.073(5), 2.083(5) and 2.033(5) Å, which are slightly shorter than those found in $Ga(6\text{-}Mepir)_3$ (2.126(4), 2.188(4) and 2.102(4)Å). The pyridyl-nitrogen in 6-Mepir is a better donor than the nitrogen in pic, due to the inductive effect of the methyl group.[89] The longer distances may occur in the better donor because of the steric hinderance associated with the methyl group. Conversely, the gallium-oxygen distances for $Ga(pic)_3$ (1.955(4), 1.936(4) and 1.955(4) Å) are larger than those of $Ga(6\text{-}Mepic)_3$ (1.939(4), 1.927(4) and 1.902(4) Å). For $Ga(6\text{-}Mepir)_3$, the nitrogen donors are formed away from the metal, while the oxygen ligands move towards the metal. This "jack-knife" effect is likely caused by the steric bulk of the methyl groups in 6-Mepir and by the necessity of the metal to maintain approximate electroneutrality.[90]

The trans isomer of $Ga(6\text{-}Mepic)_3$ is favoured because of the steric problems associated with orienting three methyl groups on an octahedral

Figure 9. An ORTEP drawing of $Ga(pic)_3$ showing the atomic numbering and thermal ellipsoids.

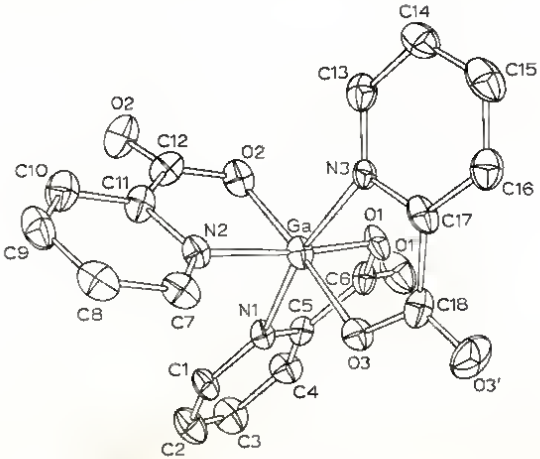
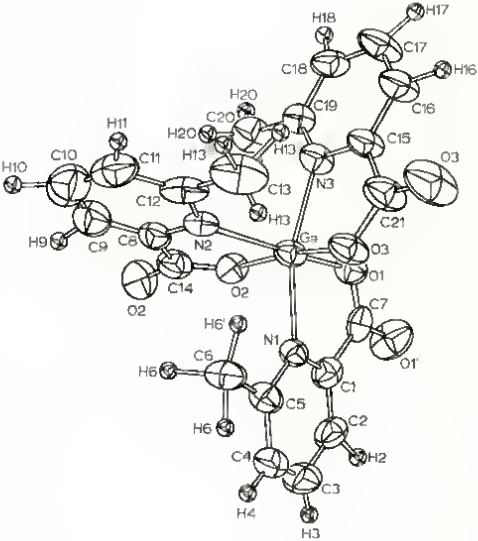

C14
C13
C15
O2
C12
O2
N3
C16
C10
C11
O1
C17
Ga
N2
O1
C9
C6
C18
C8
C7
N1
C5
O3
O3'
C1
C4
C2
C3

Figure 10. An ORTEP drawing of $Ga(5\text{-Mepic})_3$ showing the atomic numbering and thermal ellipsoids.


H17
H18
C17
C18
H16
H20
C19
C16
C20
H11
H20
H13
H13
C15
O3
H10
C10
C11
N3
C13
C12
H13
C21
H9
C9
C8
N2
Ga
O3
O1
C14
O2
O2
C7
H6'
N1
O1'
C6
H6
C1
C5
H6
C2
C4
H2
C3
H4
H3

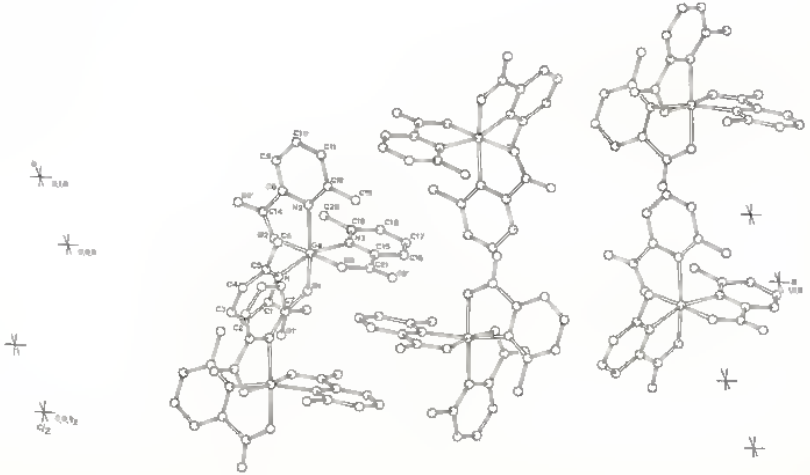
face as in the cis isomer. The cis isomer of $Ga(pic)_3$ should not be as unstable as that of $Ga(6\text{-Mepic})_3$ since GaL_3^{+3}, L = bipy, phen species exist.[19,20] However, with three carboxylate oxygens on an octahedral face, dipole-dipole interactions may destabilize the cis isomer with respect to the trans isomer.

In both these structures, we, again, note a cis effect as in $Ga(tfacac)_3$. In $Ga(pic)_3$ O2 is significantly shorter than O1 and O3 (t_g = 3.36, 3.36, respectively)[91] and N3 significantly shorter than N1 and N2 (t_g = 5.66, 7.07, respectively)[91] This differs from $Ga(6\text{-Mepic})_3$, in which O3 and N3 are significantly shorter (t_g = 6.54, 4.07 for O1 and O2 versus O3, t_g = 4.24, 15.2 for N1 and N2 versus N3)[91] These differences in the cis distortion are likely related to the steric bulk of the methyl group in 6-Mepic.

In both $Ga(pic)_3$ and $Ga(6\text{-Mepic})_3$, we have three seemingly identical ligands whose structural parameters are not equivalent. In the former compound, ligand 2 (that containing N2) has the greatest twist of the carboxylate group relative to its respective pyridine ring (9°40' versus 1°27' and 1°58' for ligands 1 and 3). This twist may cause N2 to move away from the metal and O2 to move towards it. Ligand 2 is also tilted 7°27' towards N1 and away from N3, causing the Ga-N1 distance to lengthen and the Ga-N3 distance to shorten. In $Ga(6\text{-Mepic})_3$, ligand 3 shows the least twist of the carboxylate group relative to its pyridine ring (4°15' versus 9°15' and 9°10' for ligands 1 and 2). All 6-Mepic ligands in $Ga(6\text{-Mepic})$ have large twists relative to the pic ligands in $Ga(pic)_3$. Therefore, in $Ga(6\text{-Mepic})_3$, the cis effect is due to the

Figure 11 A packing diagram for $Ga(pic)_3 \cdot H_2O$. The c glide translation is omitted for clarity.

Figure 12. A packing diagram of $Ga(6\text{-Mepic})_3$.


0,1,0
0,0,0
0,0,½
c/2
C12
C11
C9
C10
C13
C8
C14
N2
C20
C19
C18
C17
B2
C6
Cu
N3
C15
C16
C21
C5
N
C4
B1
C3
C1
C2
C7

smaller distortion of one ligand. Ligand 2 is also tilted towards N1 and this has the same result as in $Ga(pic)_3$. The nature of the cis effect in $Ga(tfmesc)_3$, $Ga(pic)_3$ and $Ga(6\text{-}Mepic)_3$ may be rationed to the electroneutrality principle [90] If the system cannot simultaneously maintain equivalent ligands and electroneutrality on the metal, then the ligands will distort.

A comparison of the packing in the two compounds is quite interesting (Figures11 and 12). Both are composed of rows of GaL_3 (L = pic, 6-Mepic), with an open space between the rows. $Ga(6\text{-}Mepic)_3$ orients the methyl groups on the pyridine rings towards this open space, while $Ga(pic)_3 \cdot H_2O$ has water molecules in the open space which hydrogen bond between O1' on O3 in different rows (OW-O1' 2.846(8)Å, HW1-O1' 1.85Å, angle OW-HW1-O1' 172°; OW-O3 2.888(7)Å, HW2-O3 1.76Å, angle OW-H 2-O3 161°). Notable in both structures is the parallel orientation of the pyridyl rings in the GaL_3 species to minimize packing.

CHAPTER 6

THE CRYSTAL AND MOLECULAR STRUCTURE OF CHLOROBIS(2-METHYLQUINOLINATO)GALLIUM(III)

The coordination chemistry of 2-Meox is dominated by steric considerations.[17] The vanadyl ion forms a VO_2-Meox compound which is trigonal bipyramidal, rather than the usual square-pyramidal.[92] Anhydrous iron(III) chloride forms $FeCl(2\text{-Meox})_2$[93] which can be hydrolyzed to μ-oxo-bis[bis(2-Meox)Fe(III)],[94] a trigonal pyramidal compound.[94] Anhydrous aluminum(III) chloride reacts with H2-Meox in methanol to form two complexes.[95] The single, μ-oxo-bis[bis(2-Meox)Al(III)],[36,96] has been determined and is trigonal pyramidal.

In aqueous solution, gallium(III) reacts with H2-Meox to form $Ga(2\text{-Meox})_3$ in nearly stoichiometric yield.[17] Methanolic solutions of anhydrous $GaCl_3$ with Na2-Meox did not yield the same compound. This behavior has no parallel in the iron(III) and indium(III) systems. Both anhydrous iron(III)[97] and indium(III) chloride react in absolute methanol with Na2-Meox to form $M(2\text{-Meox})_3$, M = Fe, In. Since the $GaCl(2\text{-Meox})_2$ is an unusual product, we undertook the determination of its structure.

Solution of Structure of $GaCl(2\text{-Meox})_2$

A sharpened, three-dimensional, Patterson function was calculated and the position of the Ga atom was determined. From subsequent Fourier syntheses, we located all non-hydrogen positions, R = 0.15. Three full-matrix least-squares cycles with individual isotropic thermal parameters

Table 34. Final positional and thermal parameters ($x10^{+4}$) for non-hydrogen atoms in $GaCl(2\text{-Meox})_2$ with their respective estimated standard deviations in parentheses. The parameters of the Ga atom are $x10^{+5}$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ga	37583(3)	-3940(8)	13966(5)	147(1)	1087(9)	432(3)	-202(7)	57(3)	56(12)
Cl	3680(1)	557(3)	2693(1)	24(1)	283(4)	55(1)	-47(2)	18(1)	-82(3)
O1	3635(2)	847(4)	465(3)	16(1)	132(7)	58(2)	-22(4)	-2(2)	41(6)
O2	3948(2)	-2269(5)	1299(3)	16(1)	12(6)	89(3)	-12(4)	15(3)	11(7)
N1	4557(2)	196(5)	1292(3)	14(1)	112(7)	40(2)	-15(4)	1(2)	0(7)
N2	2981(2)	-1195(6)	1277(3)	14(1)	124(8)	43(3)	-18(5)	5(3)	2(7)
C1	5003(2)	-203(7)	1712(4)	15(1)	141(9)	47(3)	0(6)	-2(3)	-19(9)
C2	5486(2)	446(8)	1506(4)	14(1)	152(9)	55(3)	-3(6)	0(3)	-13(12)
C3	5496(2)	1499(8)	909(5)	15(1)	135(10)	57(4)	-16(6)	10(3)	-7(11)
C4	5025(2)	1944(7)	473(4)	15(1)	102(9)	42(3)	-7(5)	9(3)	-21(9)
C5	4986(3)	3050(8)	-146(5)	20(1)	131(11)	64(4)	-19(6)	22(4)	31(11)
C6	4510(3)	3398(8)	-529(5)	22(2)	160(11)	64(4)	-9(7)	2(4)	63(12)
C7	4041(3)	2670(7)	-336(4)	20(1)	138(10)	54(4)	-11(6)	-6(4)	44(10)
C8	4063(2)	1587(6)	261(4)	16(1)	103(9)	45(3)	-8(6)	9(3)	0(9)
C9	4559(2)	1243(6)	681(4)	16(1)	92(8)	35(3)	-11(5)	8(3)	-8(8)

Table 34, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C10	4993(3)	-1333(9)	2410(5)	26(1)	178(12)	59(4)	-17(7)	- 9(4)	99(12)
C11	2507(3)	- 599(8)	1256(4)	15(1)	168(13)	57(4)	-21(7)	6(3)	8(11)
C12	2047(3)	-1429(9)	1210(5)	14(1)	177(12)	96(6)	-14(7)	3(4)	29(13)
C13	2080(3)	-2853(8)	1183(5)	13(2)	159(13)	95(5)	-39(7)	- 1(4)	36(14)
C14	2578(3)	-3505(8)	1204(4)	18(1)	128(11)	60(4)	-26(7)	3(4)	8(10)
C15	2663(3)	-4959(7)	1202(6)	21(2)	143(12)	101(5)	-42(7)	8(5)	-7(11)
C16	3160(3)	-5461(8)	1211(6)	30(2)	113(11)	105(6)	-30(8)	27(5)	-3(13)
C17	3610(3)	-4592(8)	1250(5)	24(2)	114(9)	88(5)	- 6(8)	22(4)	-7(13)
C18	3543(3)	-3175(7)	1268(4)	17(1)	110(9)	57(4)	-19(6)	9(3)	14(10)
C19	3022(2)	-2637(7)	1253(4)	16(1)	118(10)	41(3)	-26(6)	7(3)	10(9)
C20	2465(3)	992(8)	1296(6)	21(2)	116(10)	104(6)	6(6)	16(5)	10(12)

Table 35. Final parameters for the hydrogen atoms in $GaCl(2\text{-Mnox})_2$. The hydrogen atom is given followed by the atom to which it is bonded. The corresponding distance (in Å), the positional parameters ($\times 10^{-3}$) and the isotropic thermal parameter (in $Å^2$) follow.

Atom	Bonded to	Distance	x	y	z	B
H2	C2	1.06	565	21	187	5.71
H3	C3	1.11	589	201	88	5.70
H5	C5	1.18	537	356	- 44	6.08
H6	C6	1.13	433	377	-118	6.51
H7	C7	1.08	369	281	- 77	6.07
H12	C12	1.19	162	- 93	105	6.50
H13	C13	1.19	167	-346	113	7.30
H15	C15	0.99	234	-553	115	7.59
H16	C16	1.05	322	-654	122	7.98
H17	C13	1.09	401	-500	133	6.96

Table 36. Observed and calculated structure factors for $CaCl(2\text{-Meox})_2$. The three columns in each group contain the values, reading from left to right, of i, $5F_{obs}$ and $5F_{calc}$. A negative F_{obs} indicates an unobserved reflection which was not included in the least-squares refinement.

Table 37 Bond lengths, non-bonded contacts and bond angles for $GaCl(2\text{-Hoax})_2$ with their estimated standard deviations in parentheses

(a) Bond Lengths (Å)

Ga Cl	2.190(2)	C9-C4	1.403(8)
Ga-O1	1.858(4)	C9-N1	1.364(8)
Ga-O2	1.862(4)	N2-C11	1.324(8)
Ga-N1	2.108(5)	C11-C20	1.525(11)
Ga-N2	2.104(5)	C11-C12	1.404(10)
N1-C1	1.320(8)	C12-C13	1.364(12)
C1-C10	1.513(10)	C13-C14	1.399(10)
C1-C2	1.417(9)	C14-C15	1.406(10)
C2-C3	1.355(10)	C15-C16	1.342(12)
C3-C4	1.395(9)	C16-C17	1.406(11)
C4-C5	1.414(10)	C17-C18	1.365(10)
C5-C6	1.346(11)	C18-C19	1.410(9)
C6-C7	1.418(10)	C18-O2	1.339(8)
C7-C8	1.374(9)	C19-C14	1.394(10)
C8-C9	1.413(8)	C19-N2	1.382(9)
C8-O1	1.341(7)		

(b) Non-Bonded Contacts (Å)

Cl-O1	3.393(5)	O2-N1	2.813(7)
Cl-O2	3.521(5)	O2-N2	2.645(7)
Cl-N1	3.172(5)	N1-N2	4.192(6)
Cl-N2	3.186(5)	C8-C10	3.418(8)
O1-O2	3.314(6)	Cl-C20	3.661(8)
O1-N1	2.658(6)	O1-C20	3.274(9)
O1-N2	2.875(7)	O2-C10	3.181(9)

(c) Bond Angles (°)

Cl-Ga-O1	113.6(1)	C7-C8-C9	118.5(6)
Cl-Ga-O2	120.4(2)	C8-C9-N1	116.2(5)
Cl-Ga-N1	95.1(1)	C8-C9-C4	121.4(5)
Cl-Ga-N2	95.8(1)	C4-C9-N1	122.4(5)
O1-Ga-O2	125.3(2)	C8-O1-Ga	114.1(4)
O1-Ga-N1	83.3(2)	Ga-N2-C11	133.0(4)
O1-Ga-N2	92.8(2)	Ga-N2-C19	107.1(4)
O2-Ga-N1	90.0(2)	C19-N2-C11	119.8(5)
O2-Ga-N2	83.4(2)	N2-C11-C20	119.5(6)
N1-Ga-N2	169.1(2)	C20-C11-C12	120.4(6)
Ga-N1-C1	132.9(4)	N2-C11-C12	120.1(6)
Ga-N1-C9	106.6(4)	C11-C12-C13	120.9(7)
C9-N1-C1	120.4(5)	C12-C13-C14	119.9(7)
N1-C1-C10	119.3(6)	C13-C14-C15	125.2(7)
C10-C1-C2	120.5(6)	C13-C14-C19	117.1(6)

Table 37, continued . . .

N1-C1-C2	119.2(6)	C19-C14-C15	117.8(6)
C1-C2-C3	121.3(6)	C14-C15-C16	119.7(7)
C2-C3-C4	119.8(6)	C15-C16-C17	122.9(8)
C3-C4-C5	124.8(6)	C16-C17-C18	119.0(7)
C3-C4-C9	116.8(6)	C17-C18-O2	123.2(6)
C9-C4-C5	118.4(6)	O2-C18-C19	118.3(6)
C4-C5-C6	120.1(7)	C17-C18-C19	118.6(6)
C5-C6-C7	121.7(7)	C18-C19-N2	115.8(6)
C6-C7-C8	120.0(6)	C18-C19-C14	122.1(6)
C7-C8-O1	122.9(6)	C14-C19-N2	122.2(6)
O1-C8-C9	118.6(5)	C18-O2-Ga	115.2(4)

Table 38. Least-squares planes for $CaCl_2(2\text{-Mexx})_2$ in orthogonal coordinates. The title and equation of the plane are given, followed by the atoms with their deviations ($x10^{-3}$) from the plane (in Å) in parentheses. The atoms used to define the plane are noted by an asterisk following the deviation

I Quinoline Ring of Ligand 1

$$-0.1817X + 0.6608Y + 0.7283Z = -0.5383$$

Ca(127), O1(-24), N1(17)*, C1(29)*, C2(-13)*, C3(-20)*, C4(-10)*, C5(15)*, C6(25)*, C7(-5)*, C8(-31)*, C9(-7)*, C10(100)

II Quinoline Ring of Ligand 2

$$-0.0363X - 0.0263Y + 0.9990Z = 1.6849$$

Ca(98), O2(-21), N2(8)*, C11(4)*, C12(-3)*, C13(-11)*, C14(-8)*, C15(19)*, C16(-1)*, C17(-5)*, C18(-7)*, C19(4)*, C20(28)

III Plane Through Cl-O1-O2

$$0.9671X + 0.2514Y + 0.0396Z = 9.0657$$

Ca(-15), Cl(0)*, O1(0)*, O2(0)*

IV Plane Through Cl-N1-N2

$$-0.2816X + 0.8499Y - 0.4455Z = -3.9216$$

Ca(20), Cl(0)*, N1(0)*, N2(0)*

V Plane Through O1-N1-N2

$$-0.2223X + 0.6523Y + 0.7246Z = -0.9930$$

Ca(197), O1(0)*, N1(0)*, N2(0)*

VI Plane Through O2-N1-N2

$$-0.0092X + 0.0103Y + 0.9999Z = 1.8535$$

Ca(171), O2(0)*, N1(0)*, N2(0)*

Dihedral angles between planes III-IV, III-V, III-VI, IV-V, IV-VI and V-VI are 85°37', 88°43', 86°6', 107°6', 115°44' and 137°10'

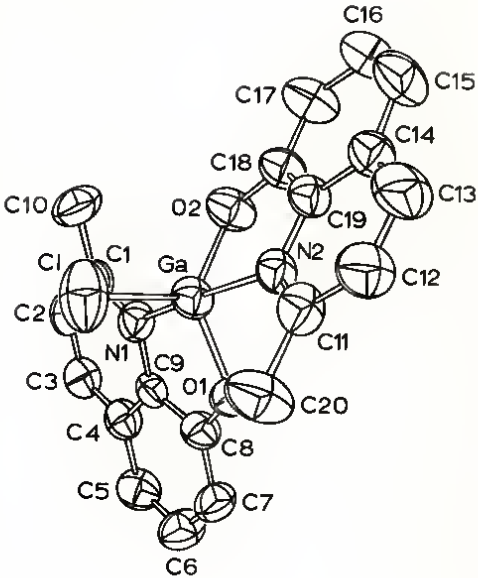
refined the model to R = 0.095. Three full-matrix least-squares cycles with individual anisotropic thermal parameters refined the model further, R = 0.052. A difference Fourier synthesis was calculated and all hydrogen atoms were found, except those on the two methyl groups. The located hydrogens were then arbitrarily assigned isotropic thermal parameters one unit higher than the atom to which they are bonded. These hydrogens were then held constant as three full-matrix least-squares cycles with individual anisotropic thermal parameters for non-hydrogen atoms were calculated. R = 0.047. A difference Fourier synthesis was again computed in order to locate the methyl hydrogen atoms. About each methyl group, a sensor of electron density existed, indicating that the hydrogen atoms were disordered. Since all shifts were now less than one-tenth of their respective estimated standard deviations, the refinement was considered complete.

Results and Discussion

Final positional and thermal parameters for the non-hydrogen atoms of $CaCl(2\text{-Meox})_2$ are given in Table 34, while the final parameters for the located hydrogen atoms are listed in Table 35. Table 36 contains calculated and observed structure factors and Table 37 contains bond lengths, non-bonded contacts and bond angles for the molecule. An ORTEP[71] diagram of the molecule showing the atomic numbering scheme used appears in Figure 13.

$CaCl(2\text{-Meox})_2$ is a molecular trigonal bipyramidal species which has normal intermolecular van der Waals contacts in the solid state.

Figure 13. An ORTEP drawing of $GaCl_3$(2-Meox) showing the atomic numbering and thermal ellipsoids.

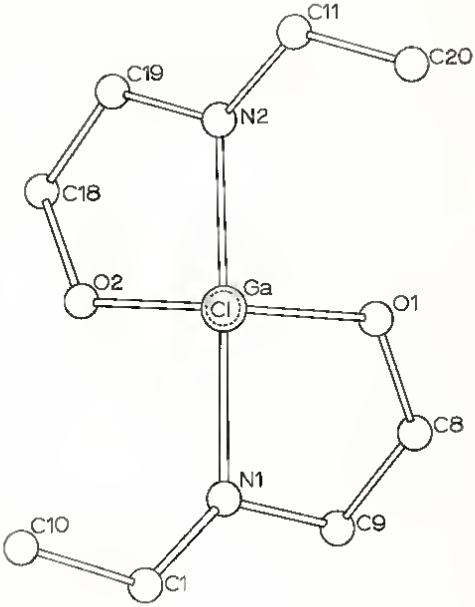

C16
C15
C17
C14
C18
C13
C10
O2
C19
N2
C1
C1
Ga
C12
C2
C11
N1
C9
C3
O1
C20
C4
C8
C5
C7
C6

The fused ten-member ring systems of the two 2-Meox ligands are planar within experimental error (Table 38). The oxygen atoms are best only slightly out of the planes of the ligands (0.074 and 0.021Å for O1 and O2, respectively), which is intermediate between $Zn(ox)(H_2O)$[98] and $Cu(ox)_2$,[99] where the oxygen atoms of the ligand range from in the plane of the ligand to 0.231Å off of the plane. Distances and angles within the ligands agree well with those found in other structures.[93,94]

The Ga-N distances (2.108(5) and 2.104(5) Å) are identical with those found in octahedral gallium complexes.[40,41] The Ga-O and Ga-Cl distances (1.858(4), 1.862(4) Å and 2.190(2) Å) are significantly shorter than the corresponding octahedral distances.[39,40,41] An interesting comparison exists between μ-oxo-bis[bis(2-Meox)M] (M = Fe, Al) and $GaCl(Meox)_2$. The Al-N distances are similar, while Al-O distances are some 0.04Å shorter than Ga-O distances. The Fe-O and Fe-N are both some 0.08Å larger than the corresponding gallium distances. Iron(III) and gallium(III) distances seem to parallel each other, while the distances of aluminum(III) and gallium(III) do not.

The orientation of the two ligands may explain the inability of $GaCl(2\text{-Meox})_2$ to readily react further in solution. The chlorine atom sits in a sheltered pocket formed by the two methyl groups on the two 2-Meox ligands. The chlorine-methyl distances (3.818(8) and 3.861(8)Å) are approximately the sum of their van der Waals radii (3.8Å),[84] making frontside attack on the chlorine atom sterically hindered. Backside attack is unlikely, since an incoming nucleophile must approach the electronegative oxygen atoms of 2-Meox ligands. Although $GaCl(2\text{-Meox})_2$

Figure 14. A view of the chelate rings and methyl groups in $GeCl(2\text{-Meox})_2$ viewed down the Ge-Cl bond


C11
C20
C19
N2
C18
O2
Ga
Cl
O1
C8
N1
C9
C10
C1

fails to react with Na2-Meox in methanol a very slow reaction occurs, with $AgNO_3$. This rules out the possibility of a free coordinate cation in methanol The small size of the gallium(iii) ion, along with the bulk of the ligand, accounts for the stability of $GaCl(2\text{-Meox})_2$, since iron(III)[57] and indium(iii), two larger ions, readily form $M(2\text{-Meox})_3$ (M = Fe,in) in absolute methanol

Another interesting comparison exists between $Ga(6\text{-Mepic})_3$ and $GaCl(2\text{-Meox})_2$. Both were prepared under identical conditions, yet 6-Mepic is capable of forming a GaL_3* species while 2-Meox is not in terms of bite, steric and electronic effects, both these ligands are extremely similar. The only difference is that 6-Mepic has rotational freedom of the carboxylate group about the pyridine ring, while the oxygen of 2-Meox is locked into position by a fused ring system. We can speculate that the GaL_3* complex can be formed only by a transition state which requires the ligand to twist considerably to accommodate a sterically hindered system. Since 2-Meox is unable to do this, $GaCl(2\text{-Meox})_2$ forms.

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* L is 6-Mepic or 2-Meox.

CHAPTER 9

THE CRYSTAL AND MOLECULAR STRUCTURES OF TRICHLORO(2,2',2''-TERPYRIDYL)INDIUM(III) AND THALLIUM(III)

Terpy is a nearly rigid ligand and, to a very large extent, its constraints dictate the geometry of the complexes it forms. Terpy metal complexes which have been characterized by x-ray diffraction include those of trigonal bipyramidal ($CoCl_2$terpy,[100] $ZnCl_2$terpy,[101] $Cd(Mn(CO)_5)_2$terpy[102]), octahedral ($GaCl_3$terpy,[41,103] $Sn(CH_3)_2Cl$terpy,[104] Cuterpy$)_2(ClO_4)_2$[105]), pentagonal-bipyramidal ($Sn(CH_3)_2(NCS)_2$terpy[106]) and tetracoordinate (Zn(terpy$)_3(ClO_4)_3$)[107] geometries. Terpy is an approximately planar ligand with a relatively small bite. The rigidity and bite of this ligand causes large distortion from idealized trigonal bipyramidal and octahedral geometries.

Ligand conformation and bite account for $GaCl_3$terpy being a distorted trans octahedral species.[41] A comparison of the Ga-Cl distances in this compound reveals that the chlorine trans to the central nitrogen, the poorest donor, is significantly closer to the metal. This was postulated as a trans effect, due, apparently, to the poor donating ability of the central nitrogen.[41] The central nitrogen, although the poorest donor, has the shortest Ga-N distance, which is due to the steric constraints of the ligand.[41] Precession photographs and vibrational spectroscopy have shown that the series MCl_3terpy (M = Al, Ga, In, Tl) are an isostructural series of compounds.[21] Since little is known about the structural chemistry of octahedral indium(III) or

thallium(III), and we would be able to study the effect of metal size on the terpy ligand, we undertook the determination of the structures of $InCl_3$terpy and $TlCl_3$terpy.

Solution of Structure of $InCl_3$terpy

Several large observed structure factors for MCl_3terpy (M = Ga,[103] In) were compared and found to vary by an approximate proportionality constant. This further indicated that the two compounds were isomorphous. A Fourier synthesis was calculated, using the fractional coordinates of all non-hydrogen atoms from the $GaCl_3$terpy structure,[103] R = 0.24. More accurate atomic positions were estimated from the Fourier and three full-matrix least-squares cycles with individual isotropic thermal parameters refined the model to R = 0.072. Three full-matrix least-squares cycles with individual anisotropic thermal parameters refined the model further, R = 0.033. A difference Fourier synthesis was calculated and the positions of all hydrogen atoms were located from it. The hydrogen atoms were then assigned isotropic thermal parameters one unit larger than the atom to which they are bonded. Three full-matrix least-squares cycles with individual anisotropic thermal parameters for non-hydrogen atoms and individual isotropic thermal parameters for hydrogen atoms further refined the model, R = 0.027. Since all shifts were one-tenth of their respective estimated standard deviations, the model was considered refined.

Solution of Structure of $TlCl_3$terpy

Several large observed structure factors for MCl_3terpy (M = In, Tl) were compared and found to differ by an approximate proportionality

Table 39. Final positional and thermal parameters ($\times 10^{+4}$) for non-hydrogen atoms in MCl_2 tarpy (M=In, Tl) with their respective estimated standard deviations in parentheses. The parameters of an atom in the In compound are given first followed by those of the corresponding atom in the Tl compound. The parameters of the In and Tl atoms are $\times 10^{+5}$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
In	17349(3)	12598(2)	21509(2)	850(4)	302(2)	340(2)	43(5)	114(4)	22(3)
Tl	16612(7)	12444(4)	21132(5)	827(8)	373(5)	357(3)	55(13)	121(7)	38(6)
Cl1	523(1)	933(1)	3485(1)	124(2)	41(1)	48(1)	30(2)	64(2)	22(1)
	421(5)	867(3)	3470(3)	159(7)	59(3)	57(5)	42(7)	84(7)	33(4)
Cl2	3119(2)	1543(1)	921(1)	219(3)	61(1)	54(1)	-29(2)	125(2)	-2(1)
	3076(6)	1549(4)	877(4)	271(10)	85(4)	70(3)	-45(9)	167(10)	-3(5)
Cl3	-970(1)	1492(1)	981(1)	118(2)	86(1)	46(1)	48(2)	-28(2)	[illegible]
	-1061(5)	1467(5)	946(3)	142(7)	136(5)	55(3)	86(10)	-20(7)	[illegible]
N1	2242(4)	-312(2)	2141(3)	126(6)	27(2)	50(2)	6(5)	64(6)	[illegible]
	2271(16)	-367(9)	2121(10)	171(26)	48(8)	61(9)	37(23)	81(28)	[illegible]
N2	4146(4)	971(2)	3333(2)	86(5)	35(2)	36(2)	22(5)	31(5)	[illegible]
	4132(15)	940(8)	3334(9)	117(20)	52(8)	52(8)	70(21)	91(21)	[illegible]
N3	2763(4)	2658(2)	2865(2)	98(5)	30(2)	38(2)	9(5)	31(6)	[illegible](3)
	2803(15)	2693(9)	2899(9)	145(23)	45(8)	48(8)	-2(22)	69(24)	[illegible](13)
C1	1182(6)	-923(3)	1537(4)	169(9)	38(3)	57(3)	-24(8)	96(9)	-22(5)
	1201(24)	-978(10)	1529(14)	311(41)	39(10)	94(13)	-107(29)	218(39)	-49(17)

Table 39, continued . . .

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C2	1377(7)	-1885(4)	1647(3)	223(12)	40(3)	83(4)	-56(9)	159(12)	-33(6)
	1359(28)	-1923(14)	1656(16)	308(50)	63(13)	81(15)	-32(40)	184(47)	- 4(23)
C3	2658(8)	-2220(3)	2417(5)	288(13)	27(3)	53(4)	-15(10)	231(13)	- 3(6)
	2710(31)	-2247(12)	2441(17)	429(56)	28(10)	115(15)	- 1(39)	377(51)	- 8(21)
C4	3816(7)	-1600(3)	3028(4)	229(11)	34(2)	69(4)	50(8)	160(11)	21(5)
	3835(27)	-1654(13)	3050(15)	248(49)	67(12)	71(14)	40(39)	155(46)	15(21)
C5	3568(5)	- 568(3)	2873(3)	134(8)	33(2)	47(3)	28(7)	94(8)	7(4)
	3612(22)	- 687(12)	2871(13)	183(36)	41(11)	63(11)	40(31)	141(34)	0(19)
C6	4692(5)	81(3)	3436(3)	119(7)	40(2)	41(3)	24(7)	74(7)	20(4)
	4687(18)	34(12)	3477(11)	142(28)	60(11)	44(9)	58(30)	95(27)	36(17)
C7	6220(6)	- 107(3)	4139(3)	133(8)	49(3)	53(3)	59(8)	58(8)	32(5)
	6188(20)	- 138(13)	4176(12)	162(31)	82(13)	67(11)	109(35)	108(32)	71(21)
C8	7114(6)	626(4)	4716(4)	98(8)	77(4)	50(3)	31(8)	10(8)	39(5)
	7090(21)	619(16)	4700(14)	118(30)	114(17)	63(13)	-13(36)	23(32)	67(24)
C9	6527(5)	1542(3)	4563(3)	108(7)	38(3)	40(2)	- 1(7)	5(7)	13(4)
	6496(18)	1320(12)	4349(11)	117(26)	68(13)	48(10)	12(26)	-12(26)	29(18)
C10	5013(9)	2701(3)	3858(3)	98(7)	39(2)	30(2)	- 5(6)	27(7)	7(4)
	5014(19)	2683(11)	3878(10)	180(30)	42(8)	35(9)	-41(27)	59(27)	-19(14)
C11	4225(5)	2643(5)	3604(3)	104(7)	35(2)	33(2)	- 6(6)	47(7)	0(4)
	4243(17)	2608(11)	3598(10)	93(23)	54(10)	38(9)	-18(24)	70(23)	-15(15)

Table 39, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C12	4952(5)	3466(3)	4061(3)	120(7)	50(3)	41(3)	-37(7)	44(7)	-27(4)
	5042(20)	3442(12)	4097(12)	186(31)	50(11)	57(10)	-40(29)	104(30)	-21(26)
C13	4190(6)	4324(3)	3752(4)	181(10)	41(3)	56(3)	-24(8)	97(9)	-20(5)
	4298(25)	4300(13)	3785(13)	243(44)	66(13)	59(12)	- 6(36)	124(40)	-21(20)
C14	2707(6)	4340(3)	2985(4)	184(9)	32(3)	66(3)	8(8)	114(9)	10(5)
	2760(23)	4331(12)	3044(13)	223(35)	39(11)	77(13)	18(32)	161(37)	24(19)
C15	2035(5)	3502(3)	2573(3)	113(7)	34(3)	56(3)	19(6)	49(7)	11(4)
	2058(20)	3511(10)	2616(13)	168(29)	40(11)	66(10)	50(25)	44(28)	21(16)

Table 40. Final parameters for the hydrogen atoms in MCl_3 tarpy (M = In, Tl). The hydrogen atom is given followed by the atom to which it is bonded. The corresponding distance (in Å), the positional parameters ($x10^3$) and the isotropic thermal parameter (in $Å^2$) follow. The data for the indium compound is given first followed by the corresponding data for the thallium compound

Atom	Bonded to	Distance	x	y	z	B
H1	C1	1.05	23	- 57	98	4 77
			*			
H2	C2	1.13	41	-233	110	5.58
			*			
H3	C3	0 97	286	-280	251	5 84
		0 93	312	-284	238	6 45
H4	C4	1.02	482	-198	344	5.14
		1.09	510	-160	352	6.43
H7	C7	1.04	666	- 80	430	4 74
		1.06	687	- 71	458	5 85
H8	C8	0.91	821	58	509	4-96
		0.97	802	46	526	6 17
H9	C9	1.08	728	209	501	5 26
		1.06	702	196	516	4.97
H12	C12	0.94	598	350	457	4 17
			*			
H13	C13	1-13	465	506	400	4.99
		1.02	503	466	444	6-09
H14	C14	1 14	223	500	253	4 81
		1-04	230	496	269	5 59
H15	C15	1.03	89	353	204	4-54
		1.15	85	366	198	5 79

* These atoms were not located

Table 41 Observed and calculated structure factors for $InCl_3$terpy
The three columns in each group contain the values, reaching from left to right, of l, $10F_{obs}$ and $10F_{calc}$. A negative F_{obs} indicates an unobserved reflection which was not included in the least-squares refinement

Table 42. Observed and calculated structure factors for $TiCl_3$terpy. The three columns in each group the values, reading from left to right, of l, $10F_{obs}$ and $10F_{calc}$. A negative F_{obs} indicates an unobserved reflection which was not included in the least squares refinement.

[illegible]

constant. This further indicated that these two compounds were isomorphous. A Fourier synthesis using the isotropic coordinates from the $InCl_3$terpy structure was calculated and non-hydrogen atomic positions were better estimated from it, R = 0.17. Three full-matrix least-squares cycles with individual isotropic thermal parameters refined the model to R = 0.069. Three full-matrix least-squares cycles with individual anisotropic thermal parameters refined the model further, R = 0.041. A difference Fourier was calculated and eight out of the eleven hydrogen atoms were found. The located hydrogen atoms were arbitrarily assigned isotropic thermal parameters one unit higher than the atom to which they are bonded and held constant, as three full-matrix least-squares cycles with individual anisotropic thermal parameters for non-hydrogen atoms refined the model to R = 0.040. Since all shifts were now less than one-fifth of their respective estimated standard deviations, the model was considered refined.

Results and Discussion

Final positional and thermal parameters for MCl_3terpy (M = In, Tl) are given in Table 39 and hydrogen parameters appear in Table 40. Calculated and observed structure factors for $InCl_3$terpy and $TlCl_3$terpy are listed in Tables 41 and 42, respectively. Bond lengths, non-bonded contacts and bond angles for MCl_3terpy, (M = In, Tl), are found in Table 43. Figure 15 is an ORTEP[71] drawing of $InCl_3$terpy which gives the atomic numbering scheme employed for MCl_3terpy (M = Ga,[103] In, Tl). The variation of individual bond lengths in MCl_3terpy with M can be seen in Figure 16.

Table 43: Bond lengths, non-bonded contacts and bond angles for MCl_3-terpy (M = In, Tl) with their estimated standard deviations in parentheses.

(a) Bond Lengths (Å)

	M = In	M = Tl
M-Cl1	2.507(1)	2.563(4)
M-Cl2	2.465(1)	2.509(5)
M-Cl3	2.396(1)	2.440(5)
M-N1	2.268(3)	2.347(13)
M-N2	2.238(3)	2.329(13)
M-N3	2.281(3)	2.383(13)
N1-C1	1.344(6)	1.35(2)
C1-C2	1.374(7)	1.36(2)
C2-C3	1.380(9)	1.39(3)
C3-C4	1.379(8)	1.37(3)
C4-C5	1.372(6)	1.40(3)
C5-N1	1.354(6)	1.39(2)
C5-C6	1.491(6)	1.49(2)
C6-C7	1.391(7)	1.39(2)
C7-C8	1.357(7)	1.40(3)
C8-C9	1.382(7)	1.37(3)
C9-C10	1.376(6)	1.36(2)
C10-N2	1.347(5)	1.39(2)
N2-C6	1.337(5)	1.34(2)
C10-C11	1.486(6)	1.47(2)
C11-C12	1.380(6)	1.44(2)
C12-C13	1.381(7)	1.38(3)
C13-C14	1.374(8)	1.42(3)
C14-C15	1.370(6)	1.37(2)
C15-N3	1.336(5)	1.34(2)
N3-C11	1.349(5)	1.33(2)

(b) Non-bonded Contacts (Å)

	M = In	M = Tl
Cl1--Cl3	3.486(1)	3.557(6)
Cl1-N1	3.301(4)	3.376(14)
Cl1-N2	3.189(4)	3.275(14)
Cl1-N3	3.413(4)	3.555(14)
Cl2-Cl3	3.539(2)	3.608(6)
Cl2-N1	3.377(2)	3.449(15)
Cl2-N2	3.378(3)	3.477(13)
Cl2-N3	3.315(4)	3.407(14)
Cl3-N1	3.723(4)	3.849(15)
Cl3-N3	3.824(4)	4.007(14)
N1-N2	2.655(5)	2.701(18)
N2-N3	2.665(5)	2.715(18)
N1-N3	4.332(5)	4.460(18)

Table 43, continued

(c) Bond Angles(°)

Cℓ1-M-Cℓ2	175.90(4)	175.5(2)
Cℓ1-M-Cℓ3	90.60(4)	90.6(2)
Cℓ1-M-N1	87.30(9)	86.8(4)
Cℓ1-M-N2	84.26(9)	83.9(3)
Cℓ1-M-N3	90.80(9)	91.7(3)
Cℓ2-M-Cℓ3	93.44(5)	93.6(2)
Cℓ2-M-N1	90.93(10)	90.5(4)
Cℓ2-M-N2	91.68(9)	91.8(3)
Cℓ2-M-N3	88.49(9)	88.2(3)
Cℓ3-M-N1	105.88(10)	107.0(4)
Cℓ3-M-N2	174.57(9)	174.1(3)
Cℓ3-M-N3	109.85(9)	112.2(3)
N1-M-N2	72.20(12)	70.6(5)
N1-M-N3	144.43(12)	140.8(5)
N2-M-N3	72.26(11)	70.3(5)
M-N1-C1	123.0(3)	121.1(11)
M-N1-C5	117.0(3)	116.9(11)
C5-N1-C1	119.4(4)	120.9(15)
N1-C1-C2	122.2(5)	120.8(18)
C1-C2-C3	118.0(5)	118.4(20)
C2-C3-C4	120.3(6)	122.7(21)
C3-C4-C5	119.0(5)	117.2(20)
C4-C5-N1	121.1(4)	119.9(17)
C4-C5-C6	123.2(4)	124.2(17)
N1-C5-C6	115.7(4)	115.8(15)
C5-C6-C7	124.8(4)	123.3(15)
C5-C6-N2	115.3(4)	116.7(14)
N2-C6-C7	119.9(4)	120.1(15)
M-N2-C6	119.1(3)	119.1(10)
M-N2-C10	119.0(3)	119.3(9)
C10-N2-C6	121.8(4)	121.6(13)
C6-C7-C8	118.5(5)	118.0(17)
C7-C8-C9	121.3(5)	121.1(18)
C8-C9-C10	118.4(4)	119.7(16)
C9-C10-N2	119.9(4)	119.6(14)
C9-C10-C11	124.7(4)	126.4(14)
N2-C10-C11	115.4(4)	113.9(13)
C10-C11-C12	122.9(4)	119.5(14)
C10-C11-N3	116.5(4)	120.8(14)
N3-C11-C12	120.6(4)	119.7(14)
C11-C12-C13	119.9(4)	117.5(16)
C12-C13-C14	119.0(5)	120.0(18)
C13-C14-C15	118.6(5)	119.2(17)
C14-C15-N3	122.8(4)	120.6(16)
C15-N3-C11	119.1(4)	122.8(14)
M-N3-C15	124.0(3)	121.4(10)
M-N3-C11	116.8(3)	115.7(10)

Table 44. Least-squares planes for MCl_2 tarpy (M = In, Tl) in orthogonal coordinates. The title and equation of the plane are given, followed by the atoms with their deviations ($\times 10^{+3}$) from the plane (in Å) in parentheses. The atoms used to define the plane are noted by an asterisk following the deviation.

I Pyridine Ring 1 (M = In)

0.7915X − 0.0078Y − 0.6111Z = −1.0392

In(−386), N1(−13)*, C1(1)*, C2(12)*, C3(−14)*, C4(3)*, C5(10)*

II Pyridine Ring 2 (M = In)

0.7132X + 0.1174Y − 0.6192Z = −1.5634

In(92), N2(12)*, C6(−9)*, C7(−1)*, C8(8)*, C9(−5)*, C10(−5)

III Pyridine Ring 3 (M = In)

0.7444X + 0.0856Y − 0.6623Z = −1.4839

In(64), N3(−3)*, C11(5)*, C12(−3)*, C13(−1)*, C14(3)*, C15(−1)*

I' Pyridine Ring 1 (M = Tl)

0.7891X − 0.0326Y − 0.6134Z = −0.9739

Tl(−500), N1(−12)*, C1(−2)*, C2(13)*, C3(−10)*, C4(−3)*, C5(14)*

II' Pyridine Ring 2 (M = Tl)

0.7057X + 0.1290Y − 0.6967Z = −1.5791

Tl(111), N2(9)*, C6(3)*, C7(−11)*, C8(8)*, C9(4)*, C10(−12)*

III' Pyridine Ring 3 (M = Tl)

0.7260X + 0.0873Y − 0.6321Z = −1.5869

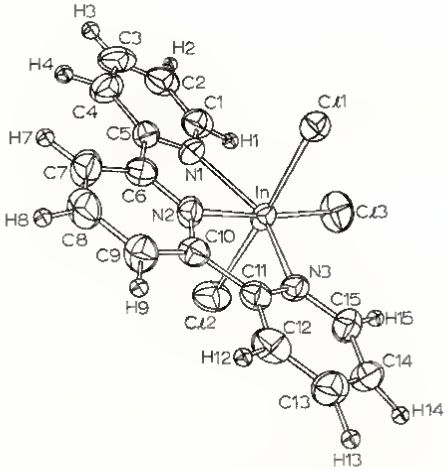
Tl(96), N3(1)*, C11(10)*, C12(−1)*, C13(16)*, C14(−5)*, C15(−4)*

Dihedral angles between planes I-II, I-III, II-III, I'-II', I'-III' and II'-III' are 9°36', 6°40', 3°2', 11°29', 8°42' and 2°48'

The MCl_3terpy (M = Ga, In, Tl) compounds are distorted trans octahedral species which have only normal van der Waals intermolecular contacts in the solid state. Distances and angles within the terpy ligands agree well with each other (Table 43) and with those previously reported.[100,101,103,104,106] All MCl_3terpy (M = Ga, In, Tl) compounds have three distinct metal-chlorine distances (2.329(2), 2.403(2), 2.235(2) Å, 2.307(1), 2.465(1), 2.396(1) Å; 2.563(4), 2.509(4), 2.440(5)Å for M-Cln: n = 1, 2, 3; M = Ga, In, Tl, respectively). The M-Cl3 distances (M = Ga, In, Tl) are consistently the shortest metal-chlorine bonds. The nitrogen trans, to Cl3, N2, is the poorest donor of the three pyridyl nitrogens and the significant shortening of the M-Cl3 (M = Ga, In, Tl) bond has been attributed to a 'trans' effect.[41] The M-Cl1 and M-Cl2 distances, (M = Ga, In, Tl), are also significantly different. Both Cl1 and Cl2 have a similar electronic environment; therefore, the difference must be due to steric interactions. These interactions occur because the terpy ligand is not planar (Table 44) and tilts towards one side of the molecule, lengthening that M-Cl distance. As metal size increases, the difference between M-Cl1 and M-Cl2, (M = Ga, In, Tl) decreases, which further indicates that this is a steric effect.

The respective metal-chlorine and metal-nitrogen distances for MCl_3terpy (M = Ga, In, Tl) correspond remarkably well with their six coordinate ionic radii, (0.62, 0.800, 0.885 Å).[5] The metal-nitrogen distances (2.115(6), 2.034(7), 2.110(7); 2.268(3), 2.238(3), 2.281(3) Å,[103] 2.347(13), 2.329(13), 2.388(13)Å for M-Nn: n = 1,2,3, M = Ga, In, Tl, respectively) are similar for N1 and N2 but are considerably shorter for

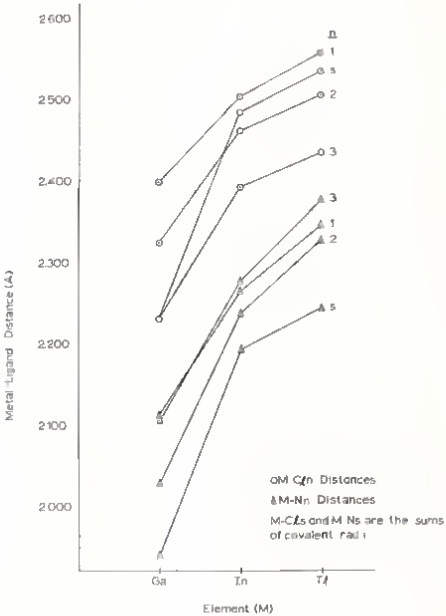
Figure 15 An ORTEP drawing of $InCl_3$terpy showing the atomic numbering and thermal ellipsoids


H3
C3
H2
H4
C2
C1
C4
Cℓ1
C5
H1
H7
N1
C7
In
C6
Cℓ3
N2
H8
C10
C8
C9
C11
N3
H9
C15
Cℓ2
H15
C12
H12
C14
C13
H14
H13

N3. The shortest metal-nitrogen distance errors with the poorest nitrogen donor, but the steric constraints of the ligand force N2 towards the metal. With increasing metal size, the difference between the M-N2 distance, (M = Ga, In, Tl) decreases with respect to the other nitrogen distances, until, with the largest metal, thallium, the difference between the average Tl -N1, Tl-N3 distance and Tl-N2 distance is not significant (t_c = 2.1). The effect of increasing metal size thus tends to diminish the steric effects of the terpy ligand and make all metal-nitrogen distances equivalent. The metal-nitrogen distances in terpy complexes, where the metals are isoelectronic, vary inversely with the charge on the metal. In $ZnCl_2$terpy[101] and $GaCl_3$terpy,[41] the metal-nitrogen distances are 2.24(1), 2.09(1) and 2.18(1) Å and 2.115(6), 2.034(7), 2.110(7)Å, respectively. Similarly, in $Cd(Mn(CO)_5)$terpy[102] and $InCl_3$terpy metal-nitrogen distances (2.475, 2.405, 2.493 Å versus 2.268(3), 2.283(3), 2.281(3)Å) decrease with increasing charge on the metal.

The structural parameters of the ligand also change slightly with increasing metal size. For MCl_3terpy (M = Ga, In, Tl), the N1-M-N3 angle decreases from 154.4(3)° to 144.4(1)° to 140.8(3)°, while the N1-N2-N3 angle increases only slightly from 105.5(3)° to 109.0(2)° to 110.9(6)°. The distortions of the ligand, reflected by increased dihedral angles between pyridyl rings, vary slightly with metal size (Table 44), which implies the ligand is rigid. The MCl_3terpy (M = Ga, In, Tl) system thus has a rigid ligand which affects the coordination sphere less with increasing metal size.

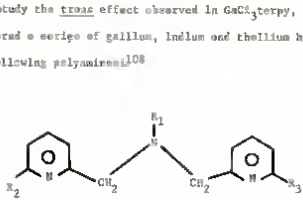
Figure 16. A plot a metal-ligand distance versus element for MCl_3terpy (M = Ga, In, Tl)


2.600
2.500
2.400
2.300
2.200
2.100
2.000
Metal-Ligand Distance (Å)
n
1
5
2
3
3
1
2
5
○M-Cℓn Distances
▲M-Nn Distances
M-Cℓs and M-Ns are the sums of covalent radii
Ga
In
Tℓ
Element (M)

CHAPTER 10

THE CRYSTAL AND MOLECULAR STRUCTURE OF DI-μ-HYDROXO-BIS{CHLORO(METHYL-(6-METHYL-2-PYRIDYLMETHYL)(2-PYRIDYLMETHYL)AMINE) GALLIUM(III)}CHLORIDE MONOHYDRATE

To study the trans effect observed in $GaCl_3$terpy, Dymock and Carty prepared a series of gallium, indium and thallium halide complexes with the following polyamines:[108]



I $R_1=R_2=CH_3$, $R_3=H$ MeMe'dpma

II $R_1=R_2=R_3=H$ dpma

Nelson and coworkers[109,110,111] had originally prepared these ligands and their corresponding transition metal halide complexes. Nickel(II), with both terpy and MeMe'dpma, forms similar trigonal pyramidal complexes.[100,112] Therefore, with the group IIIA halides, MeMe'dpma was expected to form adducts similar to those of terpy.[41] The reaction of $GaCl_3$ with MeMe'dpma produced a well-formed, colourless, crystalline product. The carbon, hydrogen and nitrogen analyses of the compound agreed well with the formulation $GaCl_3$MeMe'dpma. The infrared spectra

recorded in the regions 1600cm^{-1} to 600 cm^{-1} and 400cm^{-1} to 200 cm^{-1} also agreed well with the $GaCl_3MeMe'dpma$ formulation. Preliminary crystallographic data gave a calculated density, based on $GaCl_3MeMe'dpma$, which compared well with the measured density. The determination of the structure was undertaken with the belief firmly implanted in our minds that we were dealing with $GaCl_3MeMe'dpma$. However, the determination of the structure led us to the correct formulation $(GaMeMe'Cl(OH))_2Cl_2 \cdot H_2O$, which also agrees well with the above data.

Solution of Structure of $(GaMeMe'dpmaCl(OH))_2Cl_2 \cdot H_2O$

A sharpened, three-dimensional, Patterson function was calculated from which the positions of the two gallium atoms were determined. Successive Fourier syntheses gave us a chloro-bridged dimeric cation with disordered pyridine rings, R = 0.25. The disorder was apparent when methyl carbons were found on both pyridyl rings. Since the ligand has only one methyl group on a pyridyl ring, and the two located methyl groups appeared at approximately half peak height for a carbon atom, they were treated as half atoms. Attempts to refine this model by least-squares methods led to unreasonably high isotropic thermal parameters for the bridging Cl atoms, unusually short gallium-bridging-chlorine distances and poor convergence, R = 0.19. A difference Fourier synthesis was calculated. Peaks of negative intensity were found where the bridging-chlorine atoms were located and two previously undetected water molecules were found. At this stage, we realized that two oxygen atoms replacing a chloride would be consistent with the analysis, partial infrared spectra and density measurement. A chloride analysis showed that there were two Cl per Ga atom. Further infrared

Table 45. Final positional and thermal parameters ($\times 10^4$) for non-hydrogen atoms in $[GaMeMe'dpmaC_7(OH)]_2$ $CH_2Cl_2 \cdot H_2O$ with their estimated standard deviations in parentheses

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cation 1									
Ga1	774(1)	967(1)	4522(1)	57(1)	43(1)	44(1)	2(1)	-22(2)	18(1)
Cl1	2462(3)	1682(3)	4875(3)	63(3)	74(3)	72(3)	- 25(4)	-35(5)	28(4)
O1	666(6)	-166(5)	5613(6)	56(6)	51(6)	55(6)	13(9)	-21(10)	18(10)
N1	186(8)	2225(8)	5693(8)	81(9)	68(8)	68(9)	- 23(14)	-24(15)	6(14)
N2	502(7)	2094(7)	3261(8)	62(8)	60(8)	86(10)	20(13)	-29(15)	68(14)
N3	1293(8)	187(7)	2856(8)	61(8)	71(8)	72(9)	16(13)	-37(14)	13(14)
C1	324(12)	2441(12)	6953(13)	94(13)	118(15)	123(17)	- 89(23)	-17(24)	38(26)
C2	-141(14)	3316(14)	7625(14)	139(18)	144(17)	137(19)	-110(28)	91(29)	-150(29)
C3	-679(14)	3931(14)	7063(17)	118(18)	134(18)	158(23)	- 45(28)	65(33)	- 95(33)
C4	-804(11)	3761(12)	5791(15)	73(13)	87(13)	185(21)	- 16(21)	19(27)	- 54(26)
C5	-310(10)	2867(10)	5161(12)	76(11)	56(10)	117(14)	5(17)	19(21)	8(19)
C6	-445(11)	2616(9)	3809(11)	88(12)	57(10)	101(13)	63(18)	-29(22)	21(19)

Table 45, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C7	1407(11)	2963(11)	3080(13)	90(12)	75(11)	145(17)	-25(19)	-26(24)	128(23)
C8	269(10)	1455(10)	2098(10)	77(11)	89(11)	48(10)	67(18)	-11(18)	27(17)
C9	973(10)	566(10)	1869(10)	64(10)	94(11)	56(11)	3(18)	- 2(17)	23(18)
C10	1275(12)	111(14)	666(12)	94(14)	169(18)	76(13)	103(26)	- 1(23)	-43(25)
C11	1801(14)	- 758(15)	525(15)	123(18)	164(19)	137(19)	102(30)	-25(31)	-60(31)
C12	2151(13)	-1171(13)	1529(15)	99(15)	121(16)	161(20)	69(25)	44(29)	-93(29)
C13	1928(11)	- 653(10)	2695(13)	71(11)	67(11)	140(16)	21(18)	-27(23)	- 3(21)
C14	2427(19)	-1027(19)	3620(19)	74(21)	74(20)	62(22)	43(33)	-75(37)	37(34)
C15	728(26)	1883(21)	7545(28)	132(31)	64(22)	151(37)	100(43)	-62(39)	18(46)
Cation 2									
Ga2	5196(1)	4132(1)	8906(1)	45(1)	46(1)	54(1)	9(1)	- 7(2)	-10(2)
Cl2	6633(3)	3760(3)	7656(3)	55(3)	85(3)	83(3)	37(4)	17(5)	-31(5)
O2	5911(5)	5333(6)	9853(6)	42(6)	55(6)	71(7)	18(9)	-10(11)	-22(10)

Table 45, continued .

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{25}
N21	4659(9)	4905(8)	7508(8)	107(11)	73(9)	68(10)	49(16)	64(17)	50(15)
N22	4078(7)	2866(7)	8199(8)	51(8)	65(8)	73(9)	11(15)	- 2(14)	- 54(14)
N23	5303(9)	2852(8)	9987(8)	99(10)	98(10)	66(10)	120(16)	- 42(17)	- 12(16)
C21	5134(17)	5683(14)	6941(16)	176(23)	130(18)	166(22)	140(52)	129(36)	-110(31)
C22	4430(15)	6186(12)	5928(12)	203(20)	115(15)	99(15)	204(29)	112(29)	142(24)
C23	3527(21)	5554(19)	5750(20)	255(33)	213(28)	196(29)	139(48)	51(50)	- 33(46)
C24	3199(19)	4677(16)	6210(16)	219(32)	188(23)	129(20)	295(45)	-163(42)	- 34(34)
C25	3754(12)	4562(12)	7134(11)	98(13)	152(16)	56(11)	157(24)	- 46(21)	- 40(21)
C26	5260(10)	3387(11)	7725(11)	62(10)	121(14)	92(15)	43(20)	- 68(21)	- 29(22)
C27	4572(11)	2093(10)	7225(11)	78(12)	83(11)	95(13)	21(19)	- 21(21)	- 75(20)
C28	3807(12)	2238(11)	9251(12)	109(14)	77(11)	102(14)	-53(21)	- 18(23)	26(21)
C29	4448(13)	2080(10)	9995(11)	144(16)	51(10)	93(14)	55(21)	76(24)	3(19)
C30	4463(18)	1143(13)	10851(18)	227(28)	79(15)	225(27)	58(32)	190(44)	- 52(52)
C31	5503(17)	1354(14)	11474(14)	242(25)	157(17)	107(17)	188(34)	- 92(34)	47(27)
C32	6266(24)	2204(22)	11304(21)	299(40)	290(55)	205(50)	263(60)	46(55)	-228(52)

Table 45, continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C33	6287(20)	2961(16)	10652(12)	339(38)	213(23)	54(13)	517(51)	9(37)	58(27)
C34	6815(75)	4050(159)	10507(98)	274(117)	2074(556)	681(214)	-1156(449)	279(248)	-1677(590)
C35	5928(19)	6315(18)	7188(18)	71(20)	69(19)	42(19)	54(32)	- 36(33)	- 12(31)
Anions and Lattice Water									
C13	1644(3)	4220(3)	185(3)	61(3)	150(4)	86(3)	49(6)	- 25(5)	[illegible]
C14	2312(3)	9753(3)	7407(4)	86(3)	120(4)	132(4)	- 28(6)	-115(6)	- 112(7)
O3	749(9)	6171(10)	8894(11)	129(11)	163(13)	195(15)	52(20)	- 24(22)	136(23)

Table 46 Observed and calculated structure factors for $[CaMeMa'dpma\,Cl(OH)]_2Cl_2 \cdot H_2O$. The three columns in each group contain the values, reading from left to right, of l, $10F_{obs}$ and $10F_{calc}$. The unobserved reflections were not included.

studies revealed a strong $(Ga-O)_{as}$ at $532cm^{-1}$. The assignment of the bridging atoms as oxygen atoms eliminated the negative electron density at the bridging atoms positions and allowed the thermal parameters of the bridging atoms to refine to reasonable values. Therefore, we were dealing with a hydroxo-bridged dimeric cation with ionic chloride and water of hydration. Three full-matrix least-squares cycles with individual isotropic thermal parameters refined this model to R = 0.11. Six least-squares cycles using the block approximation with individual anisotropic thermal parameters further reduced the R to 0.070. The structure is disordered, as no attempt was made to locate hydrogen atom positions and, since all shifts were less than one-fifth of their respective estimated standard deviations, the model was considered refined.

Results and Discussion

Final positional and thermal parameters for $[GaMeMe'dpmaCl(OH)]Cl_2 \cdot H_2O$ are listed in Table 45. Calculated and observed structure factors are found in Table 46 and Table 47 contains bond lengths, non-bonded contacts and bond angles for the compound. An ORTEP[71] diagram of the cation is given in Figure 17. Figure 18 is a packing diagram which gives the atomic numbering scheme used.

The structure consists of two dipositive dimeric hydroxo-bridged cations situated on centres of symmetry and packed together with water molecules and chloride ions. The dimer consists of two octahedral gallium atoms bridged through cis asymmetrically bonded hydroxo groups, the ligand, MeMe'dpma,(I), occupies a meridional edge and a chloride is

Table 47. Bond lengths, non-bonded contacts, and bond angles for $[CaMeMe'dpmaCl(OH)]_2CH_2 \cdot H_2O$ with their estimated standard deviations in parentheses.

(a) Bond Lengths (Å)

Cation 1		Cation 2	
Ga1-Cl1	2.311(4)	Ga2-Cl2	2.289(3)
Ga1-O1	1.902(7)	Ga2-O2	1.913(7)
Ga1-O1'	2.009(7)	Ga2-O2'	2.024(7)
Ga1-N1	2.099(9)	Ga2-N21	2.100(10)
Ga1-N2	2.132(9)	Ga2-N22	2.127(9)
Ga1-N3	2.088(9)	Ga2-N23	2.083(10)
N1-C1	1.41(2)	N21-C21	1.44(2)
C1-C2	1.42(2)	C21-C22	1.61(3)
C1-C15	1.19(3)	C21-C35	1.14(3)
C2-C3	1.34(3)	C22-C23	1.34(3)
C3-C4	1.39(2)	C23-C24	1.24(3)
C4-C5	1.44(2)	C24-C25	1.41(3)
C5-N1	1.30(2)	C25-N21	1.35(2)
C5-C6	1.51(2)	C25-C26	1.46(2)
C6-N2	1.52(2)	C26-N22	1.48(2)
N2-C7	1.49(2)	N22-C27	1.52(2)
N2-C8	1.47(1)	N22-C28	1.49(2)
C8-C9	1.51(2)	C28-C29	1.47(2)
C9-N3	1.35(2)	C29-N23	1.36(2)
C9-C10	1.43(2)	C29-C30	1.54(2)
C10-C11	1.34(2)	C30-C31	1.57(3)
C11-C12	1.40(2)	C31-C32	1.35(3)
C12-C13	1.40(2)	C32-C33	1.22(3)
C13-C14	1.40(3)	C33-C34	1.43(2)
C13-N3	1.39(2)	C33-N23	1.52(3)

(b) Non-Bonded Contacts (Å)

Cl1-O1	3.134(8)	Cl2-O2	3.109(7)
Cl1-N1	3.160(11)	Cl2-N21	3.121(12)
Cl1-N2	3.364(10)	Cl2-N22	3.378(10)
Cl1-N3	3.119(10)	Cl2-N23	3.159(10)
O1-O1'	2.396(10)	O2-O2'	2.406(10)
O1-N1	3.077(12)	O2-N21	3.149(12)
O1-N3	3.120(11)	O2-N23	3.055(12)
O1'-N1	2.926(12)	O2'-N21	2.958(11)

O1'-N2	2.943(11)	O2'-N22	2.934(11)
O1'-N3	2.928(12)	O2'-N23	2.889(13)
N1-N2	2.661(13)	N21-N22	2.674(13)
N2-N3	2.674(13)	N22-N23	2.651(14)

(c) Bond Angles (°)

Cl2-Ga1-O1	95.6(2)	Cl2-Ga2-O2	95.0(2)
Cl2-Ga1-O1'	171.1(2)	Cl2-Ga2-O2'	170.3(2)
Cl2-Ga1-N1	91.4(3)	Cl2-Ga2-N21	90.5(3)
Cl2-Ga1-N2	98.3(3)	Cl2-Ga2-N22	99.7(3)
Cl2-Ga1-N3	90.2(3)	Cl2-Ga2-N23	92.4(3)
O1-Ga1-O1'	75.5(3)	O2-Ga2-O2'	75.3(3)
O1-Ga1-N1	100.4(3)	O2-Ga2-N21	103.3(4)
O1-Ga1-N2	166.0(3)	O2-Ga2-N22	165.1(3)
O1-Ga1-N3	102.8(3)	O2-Ga2-N23	99.6(4)
O1'-Ga1-N1	90.8(3)	O2'-Ga2-N21	91.6(3)
O1'-Ga1-N2	90.5(3)	O2'-Ga2-N22	90.0(3)
O1'-Ga1-N3	91.2(3)	O2'-Ga2-N23	89.4(3)
N1-Ga1-N2	78.0(4)	N21-Ga2-N22	78.5(4)
N1-Ga1-N3	156.5(4)	N21-Ga2-N23	156.5(4)
N2-Ga1-N3	78.6(4)	N22-Ga2-N23	78.1(4)
Ga1-O1-Ga1'	104.5(3)	Ga2-O2-Ga2'	104.7(4)
Ga1-N1-C1	126.0(8)	Ga2-N21-C21	128.3(10)
Ga1-N1-C5	114.6(8)	Ga2-N21-C25	111.8(8)
C5-N1-C1	119.4(11)	C25-N21-C21	120.0(12)
N1-C1-C2	119.1(13)	N21-C21-C22	110.9(14)
N1-C1-C15	125.3(19)	N21-C21-C35	121.0(19)
C15-C1-C2	115.3(20)	C35-C21-C22	128.0(19)
C1-C2-C3	119.0(16)	C21-C22-C23	110.9(17)
C2-C3-C4	123.4(16)	C22-C23-C24	126.7(23)
C3-C4-C5	115.0(14)	C23-C24-C35	117.8(20)
C4-C5-N1	124.1(12)	C24-C25-N21	125.3(14)
N1-C5-C6	118.3(11)	N21-C25-C26	120.1(12)
C4-C5-C6	117.5(11)	C24-C25-C26	114.6(14)
C5-C6-N2	106.1(10)	C25-C26-N22	108.0(10)
C6-N2-C7	110.1(9)	C26-N22-C27	111.8(9)
C6-N2-Ga1	106.2(7)	C26-N22-Ga2	108.4(7)
C6-N2-C8	109.6(9)	C26-N22-C28	108.5(9)
C7-N2-Ga1	111.8(7)	C27-N22-Ga2	111.7(7)
C7-N2-C8	111.3(9)	C27-N22-C28	109.6(9)
Ga1-N2-C8	107.8(7)	Ga2-N22-C28	106.7(7)
N2-C8-C9	108.4(9)	N22-C28-C29	107.9(11)
C8-C9-N3	117.3(10)	C28-C29-N23	117.8(12)

C8-C9-C10	122.6(11)	C28-C29-C30	127.2(12)
N3-C9-C10	120.1(11)	N23-C29-C30	115.1(13)
C9-C10-C11	119.9(14)	C29-C30-C31	108.4(15)
C10-C11-C12	121.2(16)	C30-C31-C32	125.8(19)
C11-C12-C13	118.1(15)	C31-C32-C33	128.0(25)
C12-C13-C14	113.9(15)	C32-C33-C34	138.9(60)
C12-C13-N3	120.7(12)	C32-C33-N23	111.1(19)
C14-C13-N3	125.4(14)	C34-C33-N23	107.1(52)
Ga1-N3-C13	126.6(8)	Ga2-N23-C33	115.4(10)
Ga1-N3-C9	113.9(7)	Ga2-N23-C29	112.9(8)
C13-N3-C9	119.5(10)	C33-N23-C29	131.7(12)

Table 48. Least-squares planes for $[GaMeMe'dpmaCl(OH)]_2Cl_2 \cdot H_2O$ in orthogonal coordinates. The title and equation of the plane are given, followed by the atoms with their deviations ($\times 10^{-3}$) from the plane (in Å) in parentheses. The atoms used to define the plane are noted by an asterisk following the deviation

I Plane Through Ligand One

0.7756X + 0.6259Y − 0.0819Z = 1.4132

N1(−180)*, N2(211)*, N3(−161)*, C1(17)*, C2(57)*, C3(−61)*, C4(−217)*, C5(−242)*, C6(−454)*, C7(1688)*, C8(−355)*, C9(−189)*, C10(−85)*, C11(−104)*, C12(−74)*, C13(−46)*, C14(165)*, C15(40)*

II Plane Through Ligand Two

0.5563X + 0.4254Y − 0.7138Z = 4.6143

N21(133)*, N22(−219)*, N23(106)*, C21(−1)*, C22(1)*, C23(149)*, C24(166)*, C25(202)*, C26(368)*, C27(−1715)*, C28(459)*, C29(260)* C30(249)*, C31(63)*, C32(−88)*, C33(−87)*, C34(97)*, C35(−145)*

III Pyridine Ring (N1, C1, C2, C3, C4, C5)

0.7449X + 0.6379Y − 0.1955Z = 0.5622

N1(−22)*, C1(12)*, C2(2)*, C3(−7)*, C4(−2)*, C5(17)*, C6(−22), C15(−68)

IV Pyridine Ring (N21, C21, C22, C23, C24, C25)

−0.5134X + 0.4910Y + 0.7038Z = 5.2553

N21(18), C21(−12)*, C22(−14)*, C23(39)*, C24(−32)*, C25(1)*, C26(61), C35(−83)

V Pyridine Ring (N3, C9, C10, C11, C12, C13)

0.7499X + 0.6572Y − 0.0755Z = 1.2384

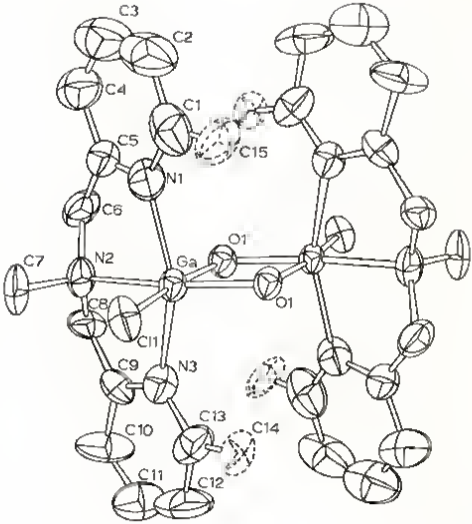
N3(−19)*, C8(−125), C9(−21)*, C10(41)*, C11(−22)*, C12(−19)*, C13(39)*, C14(219)

VI Pyridine Ring (N23, C29, C30, C31, C32, C33)

−0.4565X + 0.5036Y + 0.7335Z = 5.8178

N23(−15)*, C28(132), C29(50)*, C30(−13)*, C31(−30)*, C32(−19)*, C33(28)*, C34(362)

Figure 17. An ORTEP drawing of $[GaMeMe'dpmaCl(OH)]_2^{2+}$ (cation 1) showing the thermal ellipsoids


C3
C2
C4
C1
C5
C15
N1
C6
O1
C7
N2
Ga
O1
C8
C11
C9
N3
C13
C14
C10
C11
C12

the sixth ligand trans to the long Ga-O bond. Due to the disordering of the ligand, distances and angles within the ligand are in very poor agreement with those found in other complexes.[112,113]

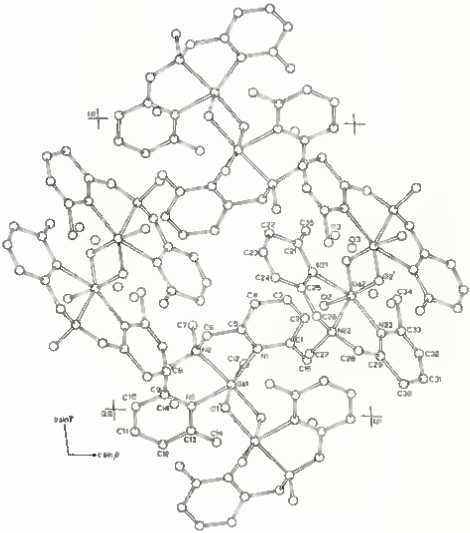
The arrangement of distances about the Ga atom in $(GaMeMe'dpma\,Cl(OH))_2Cl_2 \cdot H_2O$ is similar to that in $GaCl_3terpy$. The trans gallium - nitrogen distances are similar in both cations (2.099(9), 2.100(10)Å versus 2.088(9), 2.083(10)Å). The Ga1-N2, Ga2-N22 distances are longer in $(GaMeMe'dpma\,Cl(OH)_2)$ than the corresponding Ga-N2 distances in $GaCl_3terpy$[41] (2.132(9), 2.127(9)Å versus 2.034(7)Å). This would be due to the greater flexibility of MeMe'dpma which allows N2 or N22 to move out and/or the superior electron-donating ability of the trans hydroxide in $(Ga(MeMe'dpma)Cl(OH))_2Cl_2 \cdot H_2O$ versus the chloride in $GaCl_3terpy$.[41] A trans effect also appears in the Ga-O distances (1.902(7), 1.913(7)Å for Ga1-O1 and Ga2-O2 versus 2.009(9), 2.100(10)Å for Ga01 and Ga2-O2), the Ga1-O1 and Ga2-O2 distances trans to N2 and N22 are shortened very significantly when compared to the Ga1-O1 and Ga2-O2' trans to chloride. This is exactly the same arrangement of distances that occurs in $GaCl_3terpy$. This gallium-oxygen distance could also be due to steric interaction with the ligand which tilts towards the long gallium-oxygen bridge bond. The Ga-Cl distances are also quite long (2.301(4) and 2.289(3)Å) compared to $Ga(bipy)_2Cl_2$ (2.265(1)Å), here are somewhat shorter than the Ga-Cl1 and Ga-Cl2 distances found in $GaCl_3terpy$[41] (2.329(3) and 2.403(2)Å).

The differences in bridging oxygen-metal distances are extremely large for $(GaMeMe'dpma\,Cl(OH))_2Cl_2 \cdot H_2O$ (0.103Å). Chromium $((((py)_2Cr(OH))_2)$[114] and copper $((bipyCu(OH))_2$,[115] $(tmmCu(OH))_2$[116]) hydroxo-bridged species all have equivalent metal-oxygen distances. This may be due to hard

donors being trans to the bridging hydroxo groups. In $(GaMeMe'dpma)Cl(OH))_2^{2+}$ the asymmetry of the bridge may be due to a trans effect. However, the orientation of the ligand towards O1' and O2' could also account for the long Ga-O1' and Ga-O2' distances.

Figure 18 is a packing diagram for this compound and shows the relationship between the cations and chloride ions and lattice water. Hydrogen bonds appear to exist between the hydroxo bridges and the ionic chloride ions (O1-Cl4, 3.068(8)Å; O2-Cl3, 3.158(8)Å). Hydrogen bonds also occur between lattice water and ionic chloride ions (Cl3-O3, 3.174(13); Cl3-O3', 3.290(13), angle Cl3-O3-Cl3', 101.2(3)°)

Figure 18. A packing diagram of $[GaMeMe'dpma(\ell(OH)]_2C\ell_2$ showing the atomic numbering



CHAPTER 11

SUMMARY OF RESULTS

The synthetic procedure used to prepare the compounds studied in this work consists of the reaction of gallium(III) chloride with three equivalents of the sodium salt of a monoanionic, bidentate ligand in a suitable solvent. The precipitation of sodium chloride from solution tends to favour the reaction energetically. The solvent used is such that the gallium compound produced remains in solution and can then be readily isolated as a pure crystalline sample. With compounds such as $Ga(acac)_3$, the above method provides no advantage over the reported synthesis.[14] However, with compounds of marginal stability in aqueous, or semi-aqueous media, the procedure described is far superior. The synthesis of $Ga(dmtc)_3$ is a case in point since Delapine[16] could not prepare a pure sample of the compound from aqueous acetone. However, from dry acetonitrile-methanol, the reaction of $GaCl_3$ with Na dmtc produced a sample of $Ga(dmtc)_3$ which melted sharply and analyzed well. Our procedure has the advantage of working under anhydrous conditions and, therefore, minimizing hydrolysis. The solution species of $GaCl_3$ in non-aqueous solvents such as acetonitrile contain coordinated chloride.[117] The reactions of these chloro-solvates of gallium(III) can lead to unexpected products such as $GaCl(2\text{-Meim})_2$.

The discussions of the structures studied in this work have emphasized steric effects as a major if not the controlling factor in

the structural parameters of these compounds. Coupled with this is the tendency of the metal to maintain approximate electroneutrality which we have used to rationalize the various distortions of ligands in a complex. Of the ten gallium(III) complexes now reported, nine are octahedral or distorted octahedral species. This is not surprising since virtually all gallium(III) compounds are four or six coordinate.[18] Five-coordinate gallium(III) compounds do exist and we have been the first to characterize a five-coordinate gallium(III) complex by x-ray diffraction. We have also reported the first structure of a hydroxo-bridged gallium(III) species. This may provide some insight into the structural factors of a host of gallium(III) and aluminum(III) hydroxo-bridged species.

The nine octahedral and one trigonal bipyramidal structures of gallium(III) compounds that have been reported all contain Ga-Cℓ, Ga-N and Ga-O bonds except $Ga(dtc)_3$. A listing of the Ga-N, Ga-O and Ga-Cℓ distances in numeric order appears in Table 49. The Ga-N distances fall into three distinct ranges: 2.18 to 2.19Å, 2.13 to 2.07Å and 2.04 to 2.03Å. Seventeen of the twenty-one Ga-N distances fall into the central range. Those distances which do not fall into the central range are greatly affected by steric constraints. The Ga-O distances occur over the smaller range, 2.02 to 1.90Å, if one neglects the much shorter five-coordinate Ga-O distances. The Ga-Cℓ distance for octahedral complexes vary from 2.40 to 2.23Å, which is only slightly more than the variation of the Ga-N and Ga-O distances. This is somewhat surprising, since Cℓ is far more polarizable than N or O. This slight variance in Ga-Cℓ distances may be due to the similarity of donors in the

Table 49 A summary of gallium-nitrogen, gallium-oxygen and gallium-chlorine distances. The respective distances are arranged in numeric order. The ligand, distance (in Å), compound and trans ligand are given.

Ligand	Distance	Species	Trans Ligand
		(a) Gallium-Nitrogen Distances	
pyridyl N	2.188(4)	$Ga(6\text{-Mepic})_3$	carboxylate O
tertiary N	2.182(5)	$GaEDTA\text{-}H_2O$	carboxylate O
tertiary N	2.132(9)	$[GaMeNe'dpmaCl(OH)]_2^{2+}$	hydroxyl O
tertiary N	2.127(9)	$[GaMeNe'dpmaCl(OH)]_2^{2+}$	hydroxyl O
pyridyl N	2.126(4)	$Ga(6\text{-Mepic})_3$	pyridyl N
pyridyl N	2.115(6)	$GaCl_2tarpy$	pyridyl N
pyridyl N	2.111(4)	$GaClpy_2Cl_2^+$	chloride
pyridyl N	2.110(6)	$GaCl_2tarpy$	pyridyl N
quinaldine N	2.108(5)*	$GaCl(2\text{-Meqx})_2$	pyridyl N
quinaldine N	2.104(4)*	$GaCl(2\text{-Meqx})_2$	pyridyl N
pyridyl N	2.102(4)	$Ga(6\text{-Mepic})_3$	pyridyl N
pyridyl N	2.100(10)	$[GaMeNe'dpmaCl(OH)]_2^{2+}$	pyridyl N
pyridyl N	2.099(10)	$[GaMeNe'dpmaCl(OH)]_2^{2+}$	pyridyl N
tertiary N	2.097(6)	$GaEDTA\cdot H_2O$	water O
pyridyl N	2.095(4)	$GaClpy_2Cl_2^+$	pyridyl N
pyridyl N	2.088(5)	$[GaMeNe'dpmaCl(OH)]_2^{2+}$	pyridyl N
pyridyl N	2.083(10)	$[GaMeNe'dpmaCl(OH)]_2^{2+}$	pyridyl N
pyridyl N	2.083(5)	$Ga(pic)_3$	carboxylate O
pyridyl N	2.073(5)	$Ga(pic)_3$	pyridyl N
pyridyl N	2.034(7)	$GaCl_3terpy$	chloride
pyridyl N	2.033(5)	$Ga(pic)_3$	pyridyl N
		(b) Gallium-Oxygen Distances	
hydroxyl O	2.024(7)	$[GaMeNe\ dpmaCl(OH)]_2^{2+}$	tertiary N
hydroxyl O	2.009(7)	$[GaMeNe'dpmaCl(OH)]_2^{2+}$	tertiary N
carboxylate O	1.996(4)	$GaEDTA\text{-}H_2O$	carboxylate O
thienyl acac O	1.971(7)	$Ga(ttfacac)_3$	thienyl acac O
perfluoro acac O	1.968(7)	$Ga(ttfacac)_3$	perfluoro acac O
thienyl acac O	1.968(7)	$Ga(ttfacac)_3$	thienyl acac O
acac O	1.964(6)	$Ga(acac)_3$	acac O
thienyl acac O	1.962(7)	$Ga(ttfacac)_3$	perfluoro acac O
acac O	1.956(5)	$Ga(acac)_3$	acac O
carboxylate O	1.955(4)	$Ga(pic)_3$	pyridyl N
carboxylate O	1.955(4)	$Ga(pic)_3$	carboxylate O
acac O	1.954(5)	$Ga(acac)_3$	acac O
carboxylate O	1.953(5)	$GaEDTA\text{-}H_2O$	tertiary N

Table 49, continued

Ligand	Distance	Species	Trans ligand
water O	1.951(6)	GaEDTA H_2O	tertiary N
acac O	1.949(5)	$Ga(acac)_3$	acac O
acac O	1.947(5)	$Ga(acac)_3$	acac O
perfluoro acac O	1.943(7)	$Ga(ttfacac)_3$	thienyl acac O
acac O	1.941(7)	$Ga(acac)_3$	acac O
carboxylate O	1.939(4)	$Ga(6\text{-}Mepic)_3$	pyridyl N
carboxylate O	1.936(4)	$Ga(pic)_3$	carboxylate O
carboxylate O	1.927(4)	$Ga(6\text{-}Mepic)_3$	carboxylate O
carboxylate O	1.924(4)	GaEDTA H_2O	carboxylate O
perfluoro acac O	1.915(7)	$Ga(trfacac)_3$	perfluoro acac O
hydroxyl O	1.913(7)	$[GaMeMe'dpmaCl(OH)]_2^{2+}$	chloride
hydroxyl O	1.902(7)	$[GaMeMe'dpmaCl(OH)]_2^{2+}$	chloride
carboxylate O	1.902(4)	$Ga(6\text{-}Mepic)_3$	carboxylate O
phenol O	1.862(4)*	$GaCl(2\text{-}Meox)_2$	---
phenol O	1.858(4)*	$GaCl(2\text{-}Meox)_2$	---

(c) Gallium-Chlorine Distances

2.403(2)	$GaCl_3terpy$	chloride
2.329(3)	$GaCl_3terpy$	chloride
2.311(4)	$[GaMeMe'dpmaCl(OH)]_2^{2+}$	hydroxyl O
2.263(1)	$GaBipy_2Cl_2^+$	pyridyl N
2.235(3)	$GaCl_3terpy$	pyridyl N
2.190(2)*	$GaCl(2\text{-}Meox)_2$	---
2.171(2)**	$GaCl_4^-$	---
2.162(2)**	$GaCl_4^-$	---

* Trigonal bipyramidal complex

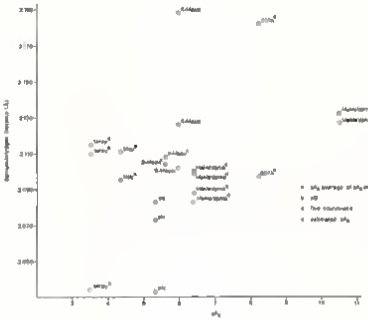
** Tetrahedral complex

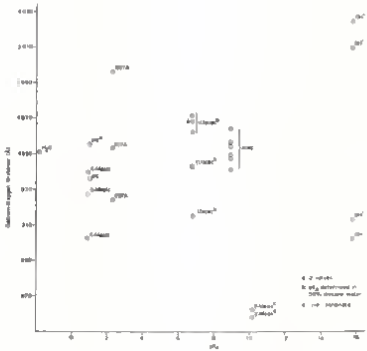
structures studied. Plots of Ga-O and Ga-N distances versus the pK_a of the respective nitrogen or oxygen ligand (Figure 19) show that both Ga-O and Ga-N distances are inversest with electron-donating ability of the same ligand atom.

The variability of metal-chlorine distances versus metal-pyridyl-nitrogen distances has been observed in zinc complexes.[118] Kennard has attributed this to metal dπ to ligand π* backbonding.[118] This does not seem to be the cause with the gallium(III) system, since tertiary amine-nitrogen donors (EDTA, MeNe'dpma) have Ga-N distances similar to Ga-N distances of pyridyl-nitrogen donors, and gallium-pyridyl-nitrogen distances vary over a larger range than zinc-pyridyl-nitrogen distances. This similarity of Ga-N distances for tertiary amine and pyridyl-nitrogen ligands may also be due to the steric constraints in the tertiary amine ligands studied. The Ga-Cl distances also decrease with decreasing coordination number (Table 45).

The electronic and steric properties which must be satisfied in the gallium(III) system are not always easily assessed. In any complex, one must satisfy both the electronic requirements of the metal and steric requirements of the ligands. Non-bonded contacts have been used to calculate geometries for tin(IV) complexes with monodentate ligands.[119] This approach has been successful for simple spherical ligands but breaks down for complicated ligands. The electronic effect observed with gallium(III) is the so-called '<u>trans</u>' effect in $GaCl_3$-terpy and $[GaMeNe'dpmaCl(OH)]_2^{2+}$. The cause and nature of this effect may be due to a tendency of the metal to maintain a symmetric

Figure 19. Plots of gallium-nitrogen and gallium-oxygen distance versus ligand pK_a 120





distribution of charge, however, further study is required to understand the effect properly.

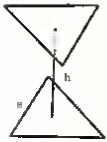
The chemistry of gallium(III) by itself may seem esoteric; however, in comparison with metals of similar size and charge (high spin iron(III) and chromium(III)), the chemistry of gallium takes on new significance. Throughout this work, we have pointed out similarities between Fe(III), Cr(III) and Ga(III). From both differences, and similarities in these three ions, one can, perhaps, assess the relative contributions of size, charge and d orbitals to their coordination chemistries

CHAPTER 12

TWIST ANGLE CALCULATIONS

Octahedral complexes formed by symmetric bidentate ligands possess C_3 rotation axes perpendicular to some faces.

(I)



(II)

The angle, ϕ, is known as the twist angle which varies from 60° for octahedral complexes to 0° for trigonal prismatic complexes. Stiefel and Brown have shown that the following relationships hold for six coordinate systems.[121]

$$(4/3)S^2\sin^2(\phi/2) + h^2 = b^2$$

$$S^2/3 + h^2/4 = a^2$$

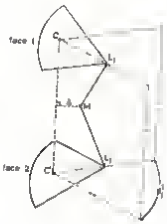
where ϕ and S are defined in diagrams (I) and (II), h is the ligand bite and a is the metal-ligand distance. The virtue of these equations is that the twist angle can be calculated from molecular distances without

knowing the positional coordinates of the atoms in the coordination sphere. Stiefel and Brown's method is based on two premises,[121] namely 1) the two threefold faces must be parallel and 2) the metal atom must lie on the line joining the centroids of the two faces. If these conditions are not met, the angle calculated is meaningless. Another criticism of Brown and Stiefel's method is that we obtain only one twist angle. This method assumes we are dealing with trigonal faces of fixed edge S; such ideality seems to be asking much of our imperfect world!

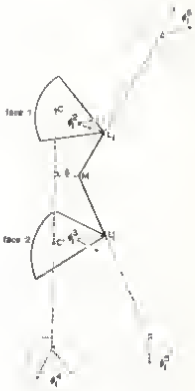
In order to compare twist angles for various compounds, we have calculated the twist angle for each ligand pair. Since several methods for calculating twist angles have been reported, we have determined ϕ in the following six ways: 1) the acute angle between planes defined by L_i, centroid 1, centroid 2 and L_i' centroid 1, centroid 2 (see Figure 20); 2) the angle between the projection of metal-L_i and metal-L_i' vectors on face 1, 3) the angle between the projection of metal-L_i and metal-L_i' vectors on face 2, 4) the angle between the projection of metal-L_i and metal-L_i' vectors on a plane orthogonal to the line joining the two centroids, 5) the angle between the projection of the metal-L_i and metal-L_i' vectors on a plane orthogonal to the metal-centroid 1 vector, and 6) the angle between the projection of the metal-L_i and metal-L_i' vectors on a plane orthogonal to the metal-centroid 2 vector. This problem of calculating of twist angle is not solely limited to octahedral complexes, but arises with any pair of nearly parallel planar e olded faces between which a metal is sandwiched, e.g., ferrocene, uranocene.

Figure 20— A schematic diagram showing the twist angle ϕ_i^n tabulated in Tables 50 and 51 The i denotes the ith ligand pair and the n signifies the nth method of calculation as given in the text. ϕ_i^1 is shown in (a), ϕ_i^n (n = 2-6) in (b) and a profile is shown in (c)

(a)



(a)



(c)

Table 51 clearly shows that twist angles for various ligand pairs vary with each other and with the mode of calculation. Therefore, Stiefel and Brown's method is not generally applicable. To use this method, one should first satisfy the conditions that u and w are small.

Differences in the mode of calculation forces us to decide whether we wish to calculate the twist of the n fold faces relative to one another or the twist about the metal. The former is calculated by method 1 and the most consistent values for twist about the metal are calculated by method 4, since methods 2,3,5 and 6 are too dependent on ω. The calculation of twist angle is best done from fractional coordinates, since assuming ideality for non-ideal systems leads to trouble, if ideality is assumed it should, at least, be checked by calculating ω and Δ.

Table 50. Twist angle calculations for π-cyclopentadienyl complexes.

Compound	$n^{\bar{x}}$	1	2	3	4	5	Reference
1) 1,1'tetramethylethylenoferrocene	1	10.4	10.3	10.8	9.7	10.4	
	2	9.6	34.5	43.2	19.6	15.5	
	3	7.5	16.2	14.3	42.0	32.0	
ω=23.2°	4	8.7	9.1	13.0	11.6	9.4	122
Δ=0.237Å	5	9.2	27.0	33.6	9.5	7.9	
	6	9.7	9.1	7.8	32.8	26.6	
	$L_iL'_i$	C1-C8	C2-C9	C3-C10	C4-C11	C5-C12	
2) α-Keto-1,1'-trimethylenoferrocene	1	6.5	5.5	5.6	5.6	5.9	
	2	10.0	19.5	11.2	7.3	4.4	
	3	3.5	4.3	2.5	14.8	12.5	[illegible]
ω=8.8°	4	6.1	5.5	6.0	5.8	5.6	
Δ=0.087Å	5	8.5	13.7	8.7	1.9	0.0	
	6	8.0	14.4	10.2	1.8	0.9	
	$L_iL'_i$	C1-C6	C2-C7	C3-C8	C4-C9	C5-C10	
3) biferrocenyl	1	16.7	16.7	17.5	15.4	19.5	
	2	12.1	13.1	19.6	20.5	20.7	
	3	18.7	18.8	16.9	13.0	18.5	
ω=2.8°	4	17.0	17.0	17.3	15.2	19.4	[illegible]
Δ=0.022Å	5	18.1	15.5	15.4	15.4	21.5	
	6	16.0	18.5	19.2	14.9	17.4	
	$L_iL'_i$	C9-C1	C10-C5	C6-C4	C7-C3	C8-C2	

Table 50, continued

Compound	m^i	1	2	3	4	5	Reference
4) α-Keto-1,5-tetra-methylenefarnacene	1	9.0	9.0	8.6	8.6	8.7	
	2	10.8	7.7	5.9	8.2	11.2	
	3	10.9	11.9	8.5	5.8	6.9	
Δ=1.6°	4	9.0	9.0	8.4	8.6	8.8	125
Δ=0.021Å	5	7.6	7.2	8.7	10.5	9.8	
	6	10.5	10.8	8.1	6.7	7.8	
	$L_1L'_1$	C1-C8	C2-C9	C3-C10	C4-C6	C5-C7	

Table 51. Twist angle calculations for octahedral complexes. $\phi_{b,h,s}$ is calculated from b, h and s and a, s/h. $\phi_{b,h,s}$ are given with their estimated standard deviations in parentheses.

	Compound	m^i	1	2	3	S(Å)	S/N	$\phi_{b,h,s}$	Reference
1)	Tris(cis-1,2-diphenylethane-1,2-dithiolato) V(III)					3.065(105)	1.00(3)	*	
		1	3.5	4.7	4.7				
		2	8.5	7.4	7.0				
		3	8.5	7.0	7.4				
		4	3.5	4.8	4.8				126
		5	3.5	3.9	5.6				
	ω=0.2°	6	3.5	5.6	3.9				
	Δ=0.015Å								
		$L_iL'_i$	S1-S1'	S2-S3	S3'-S2'				
2)	Tris(cis-1,2-diphenylethane-1,2-dithiolato) Re(III)					3.05(7)	1.01(2)	*	
		1	4.0	4.0	0.1				
		2	5.6	8.9	4.2				
		3	5.5	7.9	3.2				
		4	3.9	6.0	0.1				127
		5	3.9	6.3	0.9				
	ω=0.7°	6	3.9	6.8	0.6				
	Δ=0.013Å								
		$L_iL'_i$	S1-S6	S2-S5	S3-S4				
3)	$W(mnt)_3^{-2}$					3.19(5)	1.07(2)	[illegible]	
		1	29.1	25.3	29.1				
		2	31.4	22.4	29.6				
		3	29.6	22.4	31.4				
		4	29.0	25.5	29.0				[illegible]
		5	29.6	25.5	28.4				
	ω=1.4°	6	28.4	25.5	29.6				
	Δ=0.012Å								
		$L_iL'_i$	S1-S3	S2'-S2	S3'-S1'				

Table 51, continued

Compound	e^1	1	2	3	S(Å)	S/N	$\Phi_{b,h,e}$	Reference
4) $Mo(mmt)_3^{-2}$	1	29.8	25.0	29.0	3.19(5)	1.06(2)	28.3(15)	
	2	32.6	21.1	30.7				
ω=1.4°	3	30.7	21.1	32.6				
λ=0.008Å	4	29.7	25.1	29.7				128
	5	30.1	25.1	29.3				
	6	29.3	25.1	30.1				
	$L_i L'_i$	S1-S3	S2'-S2	S3'-S1'				
5) $Co(dsrc)_3$	1	44.5	42.1	44.5	3.39(5)	1.41(2)	43.7(6)	
	2	44.1	42.4	44.5				
ω=0.4°	3	44.5	42.4	44.1				
λ=0.006Å	4	44.4	42.2	44.4				82
	5	44.1	42.2	44.6				
	6	44.6	42.2	44.1				
	$L_i L'_i$	S2-S2'	S2-S2'	S3'-S1'				
6) Tris(ethylthioxanthate)Co(III)	1	43.3	40.4	41.2	3.55(6)	1.43(2)	41.7(8)	129
Fusions (1)	2	43.9	39.4	41.6				
	3	44.6	40.8	39.5				
	4	43.7	40.2	41.1				
ω=1.9°	5	43.9	40.9	40.1				
λ=0.020Å	6	43.4	39.4	42.1				
	$L_i L'_i$	S1-S2	S5-S4	S7-S8				

Table 31, continued —

Compound	e^{1}	1	2	3	S(Å)	S/H	$\phi_{s.h.m}$	Reference
7) Tris(ethylthioxanthate) Co(III) Fmeiriem (2)	1	44.0	40.9	41.5	3.55(5)	1.43(2)	42.2(7)	
	2	44.3	39.1	42.8				
	3	43.4	40.7	40.3				
ω=2.2°	4	44.1	40.9	41.4				[illegible]
Δ=0.006Å	5	43.9	41.2	41.3				
	6	44.3	40.6	41.5				
	$L_iL'_i$	S11-S12	S13-S14	S17-S18				
8) $In(detc)_3$	1	30.9	38.6	30.9	3.84(14)	1.45(3)	34.1(12)	
	2	31.6	41.9	26.4				
ω=5.0°	3	26.4	41.9	31.6				
Δ=0.019Å	4	30.6	38.9	30.8				[illegible]
	5	30.0	38.9	31.6				
	6	31.6	36.9	30.0				
	$L_iL'_i$	S2-S1	S3-S3'	S1'-S2'				
9) $In(pmtc)_3$	1	30.8	33.8	32.4	3.8(1)[illegible]	[illegible]	[illegible]	
	2	27.6	37.5	33.4				
	3	30.1	38.6	29.9				
ω=3.1°	4	31.0	33.8	32.2				[illegible]
Δ=0.014Å	5	31.4	33.1	32.5				
	6	30.6	36.4	31.8				
	$L_iL'_i$	S11-S12	S3-S2	S21-S20				

Table 51, continued

Compound	n^i	1	2	3	S(Å)	S/H	$\phi_{b.h.a}$	Reference
10) $Cr(oxalato)_3^{-2}$	1	44.7	51.0	42.1	2.86(14)	1.25(6)	45.8(36)	
	2	57.9	41.3	38.4				
ω=4.8°	3	57.6	47.3	32.9				
Δ=0.024Å	4	45.1	50.3	42.2				130
	5	46.3	50.6	40.8				
	6	43.8	50.1	43.7				
	$L_iL'_i$	01-02	05-06	09-010				
11) $Cu(phan)_3^{2+}$	1	55.8	50.2	51.3	3.18(17)	1.46(8)	[illegible]	
	2	46.3	56.0	52.3				
	3	48.1	49.9	57.0				
ω=6.3°	4	54.2	50.9	51.7				[illegible]
Δ=0.052Å	5	54.0	48.2	54.4				
	6	54.7	53.4	48.9				
	$L_iL'_i$	N1-N3	N5-N2	N4-N6				
12) $U(acac)_3$	1	56.1	55.8	54.2	2.79(2)	1.21(1)	55.5(11)	
	2	58.2	54.2	54.0				
ω=1.7°	3	56.5	56.2	53.8				
Δ=0.007Å	4	56.3	55.6	54.5				64
	5	56.4	56.0	54.1				
	6	56.3	55.2	55.0				
	$L_iL'_i$	01-02	03-04	05-06				

Table 51. continued

Compound	n^i	1	2	5	S(Å)	S/E	$\theta_{h,h,s}$	Reference
13) $Fe(acac)_3$	1	58.6	54.6	54.6	2.81(7)	1.22(3)	56.2(24)	
	2	59.3	51.4	57.0				
ω=5.7°	3	60.9	56.7	50.0				
Δ=0.010Å	4	58.7	55.0	54.3				68
	5	58.1	55.5	54.6				
	6	59.3	54.6	54.0				
	$L_iL'_i$	01-02	03-04	06-05				
14) CrN_3C_3	1	62.5	57.8	57.7	2.65(22)	1.03(9)	60.7(59)	
	2	66.2	59.1	52.7				
ω=3.5°	3	64.4	55.7	57.8				
Δ=0.031Å	4	63.6	57.0	57.5				15[illegible]
	5	63.1	55.8	59.2				
	6	64.3	58.5	55.4				
	$L_iL'_i$	N1-C2	N2-C3	N3-C1				

* This angle was unable to be calculated since the parameters were beyond the range of the function.

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